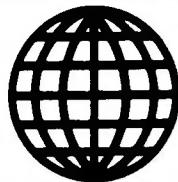


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Image Sensor for Image Scanner

43067185a Tokyo SENSA GIJUTSU in Japanese Jul 89 pp 18-22

[Article by Mitsuo Togashi, Matsushita Denso Co.: "Active Use of Image Sensor in Image Scanner"]

[Excerpts] Along with the progress in office automation (OA) in recent years, equipment for handling images and documents such as copying machines, facsimiles, and word processors has entered the stage of combining or unifying functions which have also significantly enhanced and expanded (Figure 1). With such a background, regarding the image input portion of OA equipment, there is strong demand for high-speed, high-resolution image sensors which are small and inexpensive. At the same time development for image scanners is also progressing very rapidly.

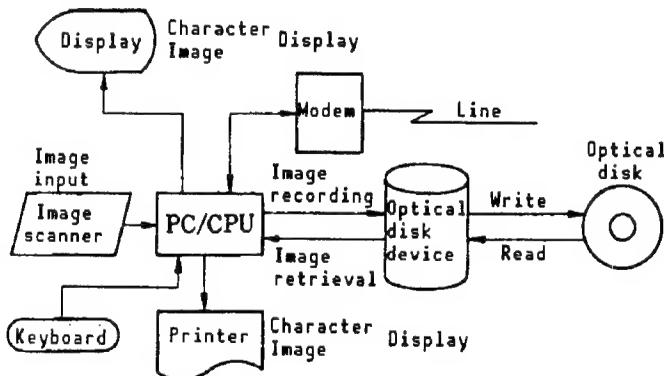


Figure 1. System Configuration of OA Equipment

In our company we have been using a contact type CdS-Se image sensor that was developed independently for the read unit of a facsimile. We have recently developed an image scanner IS-125 which is loaded with a contact type CdS-Se image sensor for high speed and high resolution.

In this paper we will discuss the method of manufacturing a CdS-Se image sensor, structure of a contact type image sensor unit, specifications of the image scanner IS-125 and tasks for future development. [Passage omitted]

2. Reduction System and Read Unit for Unmagnified System

A CCD line image sensor that uses IC technology has now reached the stage where it is able to handle 10,000 picture elements per chip through miniaturization for yield improvement of LSI and improvement of processing technology. However, due to the miniaturization of the image sensor, demands for the lens and the light source illumination in the read unit of the reduction system are becoming great. Nonetheless, image scanners are requiring high performance, multifunction, small size and profitability in order to deal with the diversified needs in OA.

In order to respond to these demands, development of a contact type image sensor that has the same width as that of the original aimed at miniaturization of the device, improved resolution of the image sensor and improved sensitivity is being pursued actively by various manufacturers. These image sensors are being applied in various ways to image input of OA equipment including facsimiles.

The structures of the reading unit of the reduction system and the unmagnified system are shown in Figures 2 and 3, respectively.

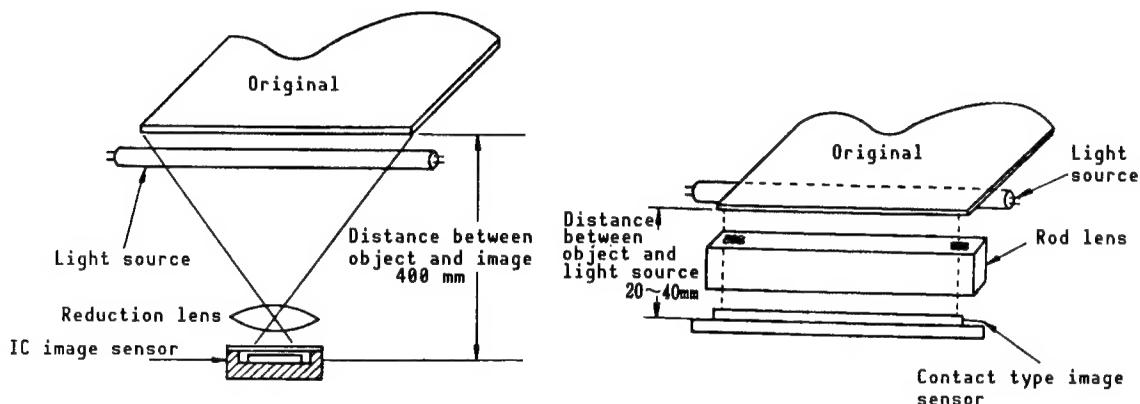


Figure 2. Reduction System Read Unit

Figure 3. Unmagnified System of Read Unit

3. Contact Type Image Sensor

The features of the contact type image sensors may be classified according to the material and the mode of photoelectric conversion (accumulation type/nonaccumulation type).

Focusing on the material, there have been developed: 1) compound thin film such as CdS solid solution; 2) α -Si thin film; 3) silicon single crystal for such things as CCD, etc.

The storage type image sensor is a device in which an optical diode formed by a thin film or a single crystal is placed in the reversed bias state to detect how much an electrical charge produced by a junction capacitor or the like is reduced during the accumulation time due to irradiation with light.

The nonaccumulation type image sensor is a device which detects the change in the electrical resistance due to light quantity as a change in the current by the use of a bias voltage, by regarding a semiconductor thin film as a resistor whose electrical conductivity is varied through irradiation with light.

The development stage of various kinds of contact type image sensors is shown in Figure 4.

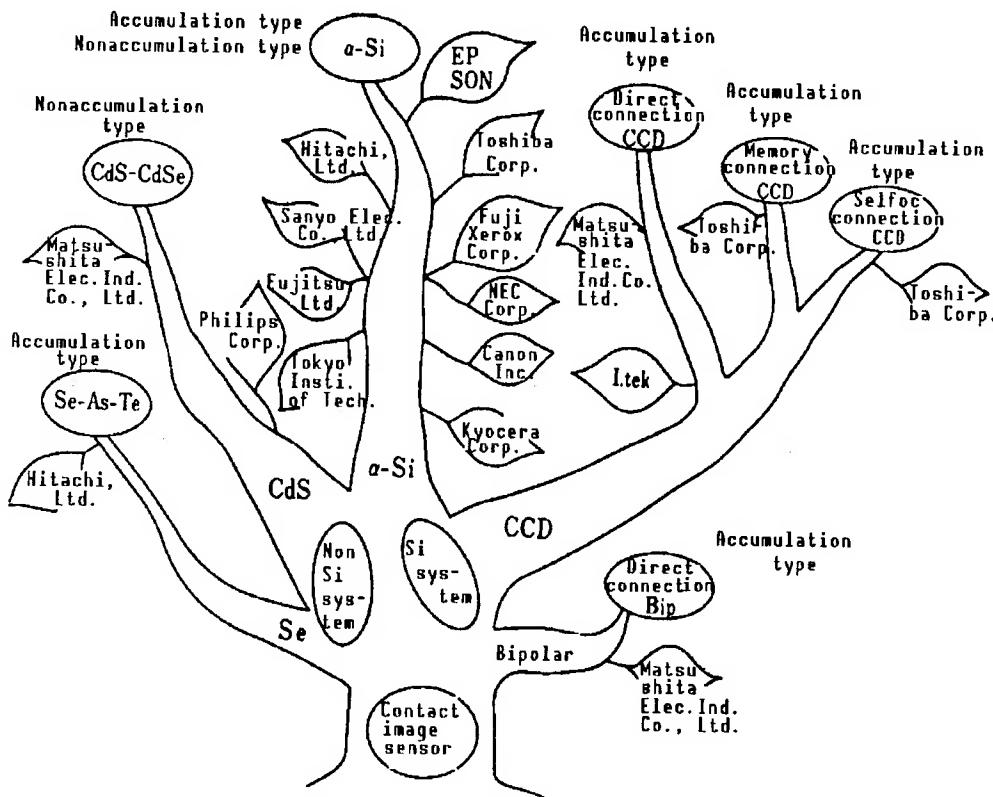


Figure 4. Development Stage of Various Kinds of Contact Type Image Sensors

Our company developed a contact type CdS-Se image sensor about 10 years ago under cooperative development with NHK.

The CdS-Se type image sensor has a simple sensor structure, extremely large photocurrent and high sensitivity. Further, it has such features as simple driving circuit and low price because it is the nonaccumulation type.

4. CdS-Se Thin Film Image Sensor

The manufacturing process of a contact type CdS-Se image sensor for an image scanner and the configuration of the sensor array will now be described.

(1) Manufacturing Process

On a glass (phosphosilicate glass) substrate, a film is vacuum-evaporated to a thickness of about 4,000 Å by using $\text{CdS}_{1-x}\text{Se}_x:\text{Cu}$ obtained by adding Cu as an impurity to a solid solution that contains CdS and CdSe in the molar ratio of $1-x:x$. The size of the element is $50 \times 175 \mu\text{m}^2$ and the Cu concentration in the film is about 0.01 mol%.

The glass substrate with a CdS-Se thin film is placed in an alumina boat that has CdS: CdCl_2 powder on the bottom; a cover is placed on the boat, and heated for about 2 hours at 500°C (activation). As a result of the activation, CdS-Se is grown into crystalline particles having a diameter of about $1 \mu\text{m}$. During the process Cl as an impurity is added, and sensitization centers and recombination centers are formed to increase the photocurrent and to decrease the dark current.

Next, an NiCr/Au counter electrode is formed in the element by the lift-off method. The counter electrodes are formed along the lengthwise direction of the activated film, facing each other at an interval of $28 \mu\text{m}$. By performing "passivation" after electrode formation, the manufacture of a $\text{CdS}_{1-x}\text{Se}_x$ optical sensor is completed.

A summary of the manufacturing process is shown in Figure 5.

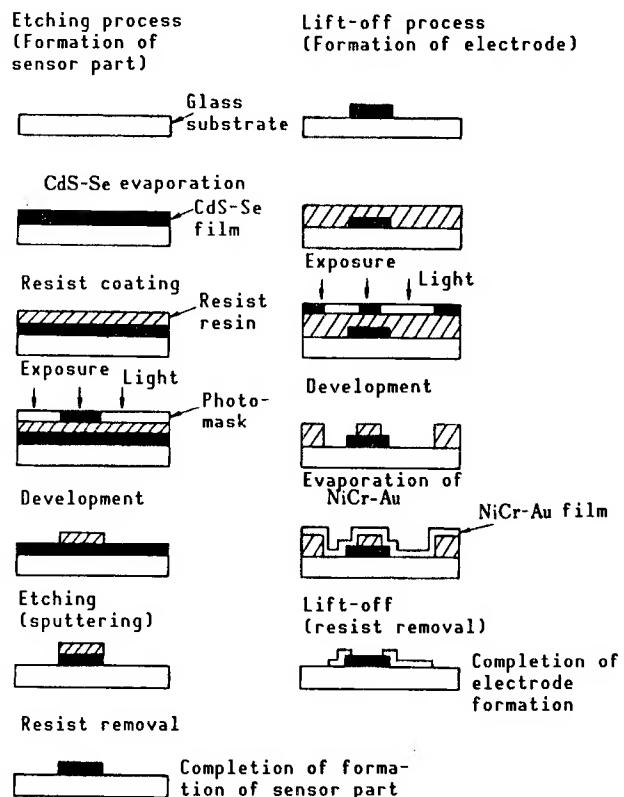


Figure 5. Manufacturing Process of Optical Sensor

(2) Sensor Array

A summary of the sensor array is shown in Figure 6. On the glass substrate, 2,560 bits of CdS-Se optical sensors are arranged linearly in the main scanning direction with element density of 300 dpi, to form the counter electrodes. The counter electrodes are divided into 80 blocks of 32 bits as a unit in order to reduce the electrode number to be connected to the read circuits, and a matrix wiring is formed by combining the individual electrodes of the corresponding bits within each block using a film lead. As a result, the matrix is made of a minimum number of connecting electrodes of a total of 112 lines consisting of 80 lines of common electrodes and 32 lines of individual electrodes (in the form of the A4 size).

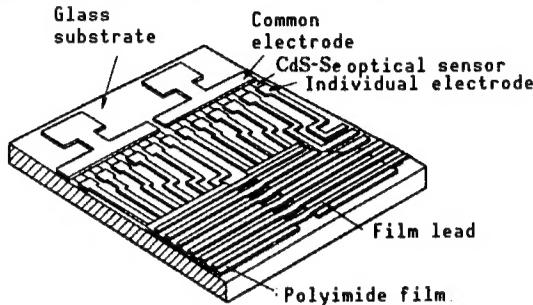


Figure 6. Contact Type CdS-Se Image Sensor

5. Contact Type Image Sensor Unit and Specifications of IS-125

The contact-type CdS-Se image sensor mounted on the image sensor IS-125 is constructed by a small-sized and lightweight unit consisting of an image sensor, an LED light source, a rod lens (SLA), a substrate for sensor driving circuit, and a substrate for image processing circuit. Its block diagram is shown in Figure 7.

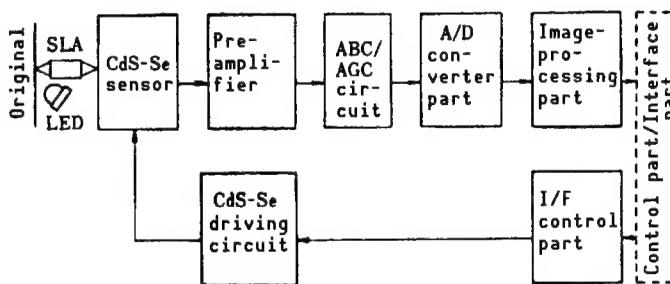


Figure 7. Block Diagram for Contact Type CdS-Se Image Sensor Unit

(1) Contact-Type Image Sensor Unit

Adoption of this unit eliminates the need for optical system adjustment such as the matching of magnification and focusing of the lens, and the resolution (MTF) is about 40 percent (6IP/mm). Further, the shading distortion caused by the light source, lens and image sensor is corrected by a shading correction circuit on the image processing circuit substrate, with the white level deviation being smaller than 10 percent.

Next, various optical system features of the contact type image sensor will be described.

From the requirement that it should be able to read the spectroscopic sensitivity of the image sensor and a stamped seal of cinnabar seal-ink, and from the viewpoint of the luminous efficiency of the LED, the emission wavelength of the LED light source was chosen to be 565 nm. The shape of the condenser lens of the LED light source is semicylindrical, and it is to suppress the formation of shades due to wrinkles in the original by utilizing a part of the base table as a reflecting plate. Figure 8 is a sectional diagram showing the positional relationship of the optical system.

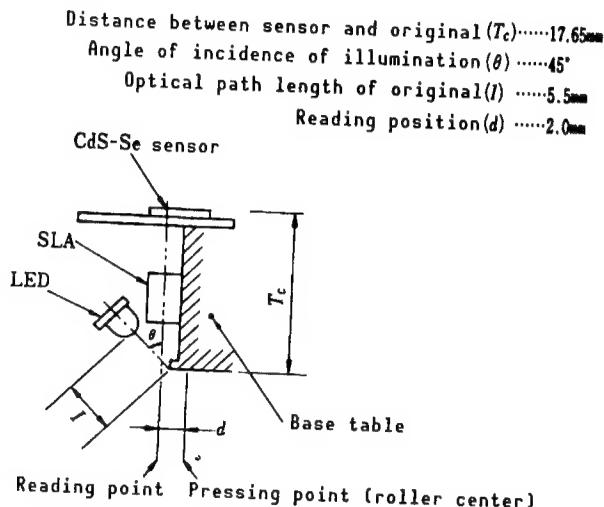


Figure 8. Sectional View of Contact-Type Image Sensor Unit

(2) Specifications of IS-125

By mounting the contact-type image sensor, IS-125 was able to realize small size, light weight, high reliability and low cost.

A summary of its specifications is shown in Table 1.

6. Future Development Problems

Along with combining and unifying OA equipment, an increasingly high degree of performance, miniaturization and profitability will be demanded of the future image scanner and image sensor.

Table 1. Summary of IS-125 Specifications

Item	Specification
Reading element	Contact type image sensor (CdS-Se)
Reading system	Sheet feed type (with ADF)
Light source	LED ($\lambda_p = 565$ nm)
Size of original	A-4 letter
Reading range	216 x 457 mm maximum
Reading resolution	300 dpi (main scanning direction)
Stoppage of reading	Arbitrary
Reading density switching	6 stages (command switching)...binary 2 stages (command switching)...dither
Gradation	Binary and dither (16 gradations), gray (16 gradations)
Reading time	8 ms/line 28.1s/A-4 300 dpi (subscanning direction) 14.1s/A-4 150 dpi (subscanning direction)
Interface	Parallel interface
Size and weight	3.6 (W) x 274 (D) x 124 (H) mm, about 6 kg

The future tasks are listed below:

(1) Improved Image Quality

- a. High-speed and high-reliability processing
- b. Halftone processing
- c. Color processing

(2) Expanded Editing Function (Rendering the System Intelligent)

(3) Reduced Size and Price

- a. Solidification of functional devices (rendering the device fully contact type and TFT)
- b. Rendering the processing circuit fully LSI.

References

1. Togashi, M., et al., "Read Unit of High-Speed and High-Resolution Facsimile," National Meeting of Television Society, 1983, paper No 16-3.
2. Ibid., "Facsimile Shading Corrector," ISSCC '84, THPM 14.3.
3. Komiya, I., "Trends of Image Sensor for Facsimile," Federation Meeting of Four Electrical Societies, 1984, paper No 19-1.
4. Togashi, M., "Application to Line Sensors," ELECTRONICS, February 1986 issue.

Remote Sensing, Ozone Lider, Measuring Global Environmental Problems

43067185b Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 33-38

[Article by Mitsuo Togashi, Matsushita Denso Co.: "Recent Technical Trends in Atmospheric Pollution Measurement"]

[Text] The system of monitoring atmospheric pollutants in this country is being called one of the best observational networks in the world partly due to the fact that it was mandated by law. However, the target materials are mainly sulfur dioxide, nitrogen oxides, carbon monoxide, photochemical oxidants and buoyant particulate substances. The observational system for substances other than these is not in a sufficiently well-maintained condition.

In particular, the current observational system concerned with global pollution problems (warming of the earth's surface, ozone holes, acid rain, etc., being reported almost daily) is supported by the steady effort of a handful of research organizations and individual researchers. It should be acknowledged that the discovery of the ozone hole in the South Pole region was a result of steady observation at Showa Base. It is regrettable that it is not widely known that this discovery was the result of going over the observed data provided by the images taken by the polar orbit satellite NIMBUS 7, which suddenly became famous.

In order to grasp the state of global atmospheric pollution, observation at one spot, as was done in the past, is useless. In particular, for medium- to long-range observation of the atmosphere over the ocean and the stratosphere, remote sensing techniques that use artificial satellites and lidar (laser radar) become important.

On the other hand, there are demands for technology that can measure diverse pollutants quickly and with high sensitivity and accuracy. This is because the pollution mechanism became more complex: not only are the direct effects of the primary pollutants of concern as in conventional cases, but also various additional reactions become of concern, and, further, concentration of interest levels are becoming lower.

Additionally, for enhanced reliability of each set of data it is necessary to have fine-grained measurements, not just the grasping of the overall situation by remote sensing.

Centered around the ozone lidar, which has attracted people's interest in recent years as a method of measuring the ozone layer in the stratosphere (measurement of vertical distribution of ozone), and the total ozone mapping spectrometer (TOMS) sensor on an artificial satellite as a method to measure the total ozone level over a wide area, the semiconductor laser infrared spectroscopy and atmospheric pressure mass spectrography will be described as methods of measuring diverse pollutants with high sensitivity and high selectivity. Lastly, I will explain recent trends in the development of gas sensors, the field that, in recent years, has experienced rapid development with high sensitivity. These sensors are expected to be used more frequently in the future to measure the atmospheric environment.

1. Ozone Observation by Remote Sensing

Conventional monitoring was conducted by placing various kinds of measuring instruments at numerous places and determining the pollution conditions of the area from the data obtained. However, there has always been a question of how to present the data, and various procedures such as the optimum arrangement of the instruments have been the subjects of debate. The remote sensing technique represented by lidar has been drawing attention as a method which will solve the above-mentioned problems by making it possible to take measurement in a spatially continuous state. However, the apparatus required is large and expensive; thus examples of installation are few. Nonetheless, remote sensing is the only means of measuring stratospheric ozone from great distances in the vertical direction and distribution of density over a wide region.

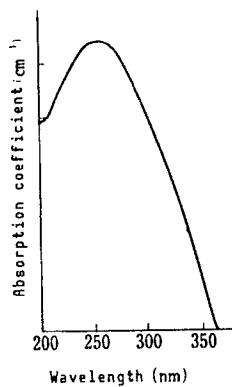


Figure 1. Absorption Coefficient of Ozone

Ozone measurement utilizing the absorption of ultraviolet rays is carried out by using the 250-340 nm wavelength of the Hartley-Huggins ozone absorption band (Figure 1). From the absorption of solar radiation by the ozone and the wavelength dependence of the scattering cross section by the atmospheric molecules, it can be seen that the scattering cross section by the atmospheric molecules does not depend too much on the wavelength in the above-mentioned range, whereas the absorption by ozone has a strong wavelength dependence. As a result, the amount of ultraviolet radiation with wavelengths smaller than 320 nm on the ground decreases rapidly. Ultraviolet radiation with wavelengths smaller than 320 nm will not reach the ground. The Dobson spectrometer has been widely used for a long time to measure total ozone levels on the ground.

It can measure two selected wavelengths of ultraviolet radiation (e.g., 325.4 nm and 305.5 nm) for which the intensities in the solar radiation in the atmosphere upper level are comparable but the absorptions by ozone change rapidly. Based on these differences in the measured value of the two wavelengths, the total amount of ozone is calculated (Figure 2).

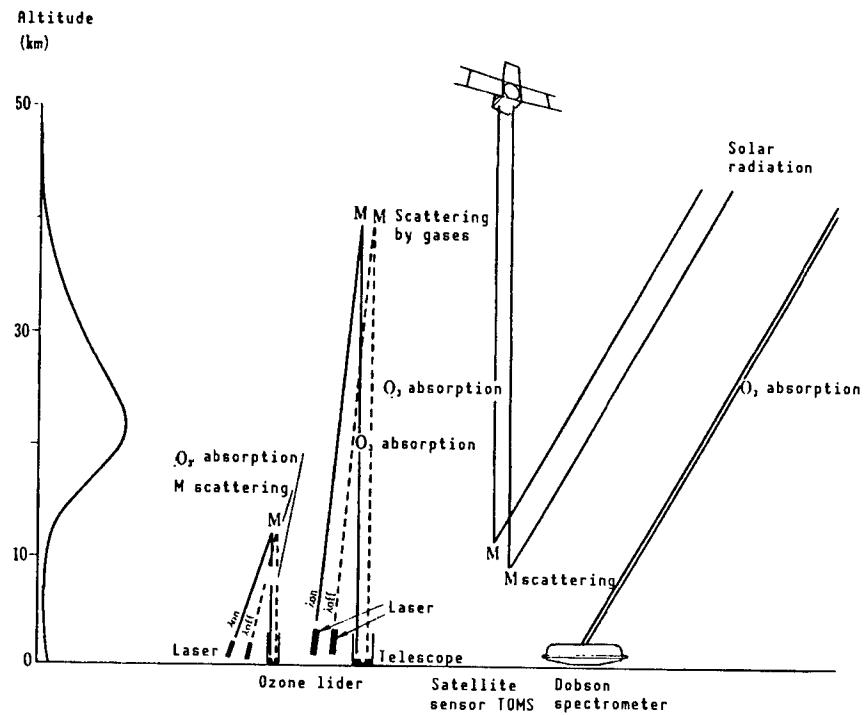


Figure 2. Conceptual Diagram for Ozone Measurement by the Use of Ultraviolet Radiation

Ozone observation using an ozone lidar or a satellite, making use of the above-mentioned technique in principle, will be described next.

(1) Ozone Lider

In the ozone lidar method, laser beams with two wavelengths--radiation with one wavelength which is absorbed strongly by ozone and radiation with another wavelength which is not absorbed strongly--are radiated into the sky, and receive the beams that come back scattered by the air or aerosols (Figure 2). The altitude (position) resolution is determined by the time during which the laser beam is emitted and the signal returns. The vertical distribution of ozone concentration is determined by taking the difference between the attenuations of signals with two wavelengths and differentiating it in the altitude direction. This method is also called differential absorption lidar (DIAL) since the gas concentration is determined from the difference in absorption.

By calling the wavelength for which the absorption by ozone is large λ_{on} and the wavelength with small absorption λ_{off} , the numbers of received photons with two wavelengths $n_{on}(z)$ and $n_{off}(z)$ from altitude z are given by

$$n_{on}(z) = C_{on} A n^0 \beta_{on}(z) z^{-2} \\ \times \exp \left[-2 \int_{\phi}^z \{ \alpha_{on}(z') + \sigma_{on} N(z') \} dz' \right] \quad (1)$$

$$n_{off}(z) = C_{off} A n^0 \beta_{off}(z) z^{-2} \\ \times \exp \left[-2 \int_{\phi}^z \{ \alpha_{off}(z') + \sigma_{off} N(z') \} dz' \right] \quad (2)$$

In the above equations, C is a constant that depends on the efficiency of the optical system and others, n^0 is the number of photons contained in the laser pulse, A is the area of the telescope, $\beta(z)$ is the coefficient of backscatter, $\alpha(z)$ is the dissipation coefficient and $N(z)$ is the ozone concentration.

From Equations 1 and 2 the ozone concentration is given by

$$N(z) = \frac{1}{2(\sigma_{on} - \sigma_{off})} \frac{d}{dz} \ln \frac{n_{off}(z)}{n_{on}(z)} + B + T \quad (3)$$

In the above, B is the corrected term for the fact that the wavelength dependence of the back scattering coefficient for the air and the aerosols and T is the correction term for laser beam by the air and the aerosols.

The ozone lidars installed at the National Institute for Environmental Pollution Research have two lidars for high altitude (15~50 km) and for low altitude (1.5~15 km), both controlled by the same computer. The wavelengths used total six, namely, three for high altitude (308, 339 and 351 nm) and three for low altitude (277, 292 and 313 nm). By providing a principal series and an auxiliary series for each wavelength, and by adding a transient digitizer for the low altitude system, wavelength optimization and dynamic range extension are realized for each altitude region. The use of multiple wavelengths is effective for correcting errors due to aerosols.

Since ozone lidar makes it possible to accurately observe the vertical distribution of ozone so that it can be used to observe seasonal variations and monitor annual variations of the ozone layer and the vertical distribution of ozone, it is also expected to play a role in demonstrating the vertical distribution of ozone concentration obtained by artificial satellites.

At present there are several ozone lidars in the world that can measure ozone concentration at high altitude with high accuracy, but observation of the stratospheric ozone by these instruments has just begun. Further, these observation networks that are concentrated in the mid-latitude zone of the northern hemisphere, must be extended in the future to many other places in the world.

(2) Artificial Satellite Sensor

TOMS is a diffraction grating spectrometer with wavelength resolution of 1 nm which was mounted on a solar synchronous polar orbital satellite NIMBUS 7 launched in 1978, and measures intensities of six ultraviolet wavelengths between 312.5 nm and 380 nm. From the analysis of wavelength dependence of

the ultraviolet intensity scattered from the atmosphere on the ground's surface and in the troposphere, the total amount of ozone column is determined. During 13.8 revolutions around the earth that the satellite makes in 1 day TOMS can draw the distribution graph of the total amount of ozone column of the entire earth except for the polar region in the winter.

The changes in the ozone concentration above the South Pole measured by TOMS are published as a colored image, and became famous as an ozone hole (spot where the ozone concentration is low) over the South Pole.

Besides TOMS, NIMBUS 7 has on board a solar backscatter ultraviolet (SBUV) instrument which can measure the vertical distribution of ozone concentration. However, due to equipment deficiencies, the measurement is now being taken by SUB/2 on satellite NOAA. In addition, the vertical distribution of ozone and aerosols and NO_2 and H_2O are being measured by a stratospheric aerosol and gas experimental instrument (SAGE) II placed on satellite ERBS.

In this country, an infrared spectrograph for atmospheric periphery is placed, in addition to a BUB, on the satellite "Ozora" to experimentally measure aerosols, H_2O , CO_2 , CH_4 , N_2O and O_3 .

2. Semiconductor Laser Infrared Spectrometer

Infrared spectroscopy is an excellent method to measure many kinds of substances using the same technique. However, in the atmosphere, there are many substances coexisting and these spectra interfere with each other, so that it is difficult to obtain measurements with high selectivity.

Therefore, the nondispersive infrared method (NDIR) was used in measuring atmospheric pollution to analyze components with relatively high concentration such as CO_2 and CO.

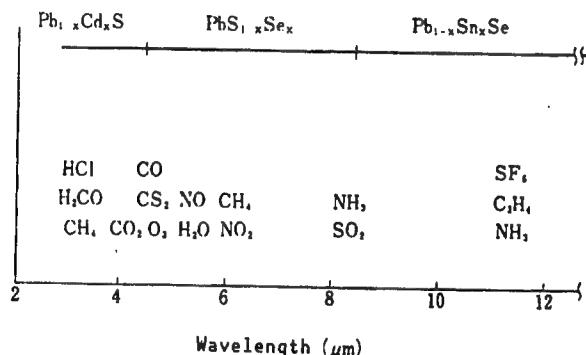


Figure 3. Range of Oscillation Wavelength of Semiconductor Laser and Measurable Substances

On the other hand, laser developments in recent years have been remarkable and lasers are being used in many fields of measurement. In infrared spectroscopy, due to variable wavelength semiconductor lasers as light sources, it is becoming possible to carry out high-resolution and high-sensitivity measurements which were difficult to realize in the past. A semiconductor laser is

an unprecedented, excellent light source in spectroscopy which has both properties of monochromaticity and wavelength variability. The semiconductor laser used in infrared spectroscopy is a ternary system (Figure 3), and the range of oscillation wavelength can be varied by changing the ratio of each constituent. The infrared spectroscopic features of the semiconductor laser are as follows:

- (1) It has a luminance which is 10^8 to 10^{11} times stronger than the conventional infrared light source.
- (2) It is possible to vary the wavelength of the radiation by changing the temperature and the inrush current of the element.
- (3) It has excellent monochromaticity.
- (4) It is possible to carry out wavelength modulation at high speed by modulating the inrush current.

Item (1) opens the way to high sensitivity and (2) makes it possible to adjust the laser beam to the absorption wavelength of the target component for observation. In addition, (3) makes high-resolution (0.0003 cm^{-1}) measurement possible, and (4) shows that it is possible to utilize various types of modulation.

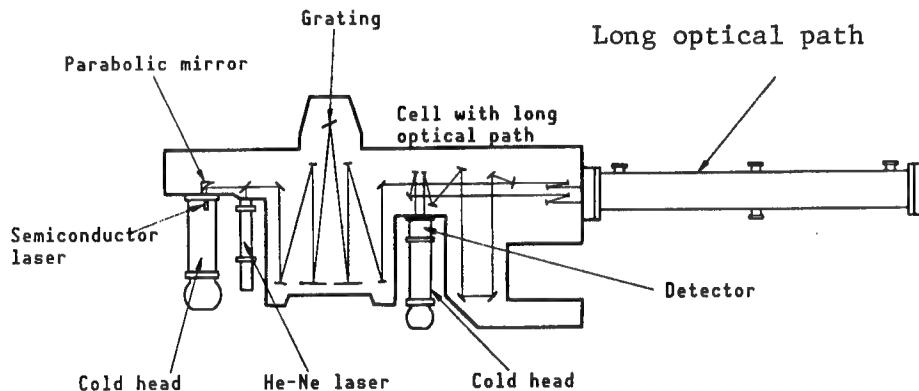


Figure 4. Example of Semiconductor Laser Infrared Spectrometer

An example of the semiconductor laser spectrometer is shown in Figure 4. In the system shown in the figure, a spectrometer is incorporated in order to select the target wavelength component alone, from a light source which is oscillating in multimode. However, as a result of improvements in recent years, it is becoming possible to obtain a beam which is close to a single mode beam so that the construction of the spectrometer can be made simpler. Further, elements that can be used at liquid nitrogen temperature are being developed, and the cooling equipment is also being made smaller.

As mentioned at the beginning, semiconductor laser infrared spectroscopy makes it possible to measure a multitude of substances with one technique, and there have so far been reported analyses of over 100 species. In a situation in which a variety of pollution components are of concern and, moreover, new

pollutants are expected to show up as at present, there are many difficulties in building measuring systems for the exclusive use of each component. Therefore, it is considered urgent to establish a method which can measure various kinds of components with one technique as the present system.

The sensitivity of the spectrometer used to be limited by the fringe noise or fluctuations in the light source. However, improvements are coming thanks to the development and improvement of optical elements and the compensation method.

3. Atmospheric Pressure Mass Spectrometer

Because ionization takes place under atmospheric pressure, the atmospheric pressure ionization (API) method was developed. This method has a satisfactory ionization efficiency and is essentially the same as the conventional CI so that it is easy to generate molecular ions. Namely, the sensitivity is high since the sample molecules are ionized by a large number of reactive ions that are generated under normal pressure. It also has an advantage that the combination with GC and LC is feasible since the system for introducing the sample is free from problems related to the vacuum.

The mass spectrometer is being used domestically for measuring the impurities in the processing gas for semiconductor manufacture. In the United States, however, the trace atmospheric gas analyzer (TAGA), which can be placed on a vehicle to measure various kinds of atmospheric pollution components while the vehicle is moving, is available commercially. The ion source is the direct introduction type API, while the mass analysis part is given an improved selectivity by tandem connection of three units of QMSs.

4. Gas Sensor

(1) Ozone Meter

Ozone sensors reportedly have a considerably higher sensitivity than that of conventional sensors, and their practical use has been awaited. Lately, an apparatus, with the trade name ozone hunter, which can measure ozone to low concentrations has become commercially available. The sensor used in this apparatus is of the following type.

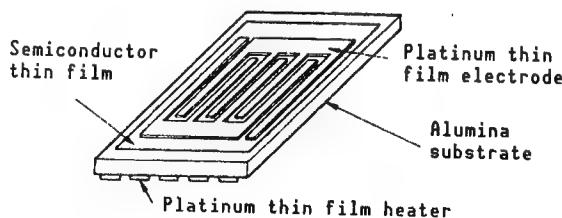


Figure 5. Structure of Ozone Sensor

The structure of the detection part consists, as shown in Figure 5, of a platinum thin film heater, an alumina substrate with platinum thin film electrodes and a semiconductor thin film formed on the platinum thin film

electrodes. The semiconductor thin film which is kept at a certain high temperature by the heater increases its resistance markedly as a result of decomposition and adsorption of an oxidizing gas (here, it is ozone). The ozone concentration can be determined by measuring the change in the resistance value.

$$\text{Resistance value} = K \cdot C \alpha \quad (4)$$

where K and α are constants and C is the ozone concentration.

This ozone measuring apparatus is small and light as can be seen from Photo 1, and can be operated by batteries. Since it has a sufficiently high sensitivity which makes it usable for ozone measurement in the ambient atmosphere, we hope it can be made into an apparatus for ambient atmosphere by incorporating an arithmetic circuit and adding a constant flow rate device.

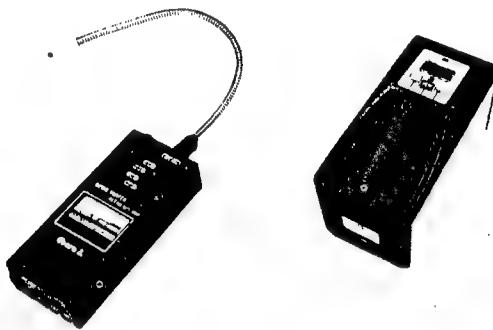


Photo 1. Ozone Meter Using Semiconductor Thin Film Sensor

Photo 2. Hydrogen Sulfide Meter Using Gold Thin Film Sensor

(2) Hydrogen Sulfide Meter

The hydrogen sulfide sensor was originally developed for mercury analysis apparatus by the atomic absorption method, but it has been modified as a gold thin film hydrogen sulfide sensor with high sensitivity for hydrogen sulfide and fast response speed by later improvement and research.

The gold thin film hydrogen sulfide sensor absorbs and stores hydrogen sulfide that exists in the sample. The concentration of hydrogen sulfide in the sample is measured by making use of the fact that electrical resistance varies in proportion to the amount of hydrogen sulfide absorbed and stored.

The appearance of the hydrogen sulfide meter commercially sold is shown in Photo 2, and its block diagram is shown in Figure 6.

When the "SAMPLE" button is pressed, sample air is first passed through a zero gas filter, and by cleaning the interior of the device with the zero gas generated, the effect of the previous measurement is eliminated, and an automatic zero calibration is carried out. Next, a three-way valve is activated to introduce a predetermined amount of sample air. Then, from the change of the electrical resistance before and after the collection of a sample, the concentration of hydrogen sulfide is computed by a microprocessor

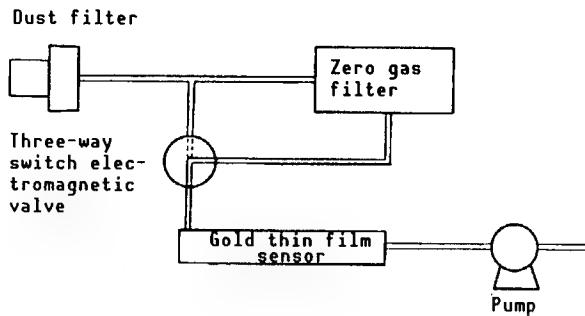


Figure 6. Block Diagram for Hydrogen Sulfide Meter Utilizing Gold Thin Film Sensor

which is displayed digitally. When the accumulated amount is saturated, the linearity of the electrical resistance response to hydrogen sulfide disappears. In this case, by heating (at 150-200°C for 10 minutes) the sensor in the presence of oxygen, hydrogen sulfide can be reused by liberating it from the gold thin film.

The sensitivity of the device is very high and it is possible to detect 1 ppb in a measuring time of 10 seconds. Further, the sensitivity to NO₂ is also high so that application to an NO₂ meter for the environment is being investigated.

The environmental problem is diverse so that it is difficult to measure all of the components of the atmosphere. Nonetheless, along with the continuation of the current atmospheric pollution observation network, it will become increasingly important to establish a system that can respond quickly to global pollution problems and wide area pollution problems, and an observational system with long-term vision. Under these circumstances, development of a new measuring technique and development of a sensor which makes it possible to measure the ambient atmosphere quickly and easily are earnestly desired.

Further, although it has not been touched upon in this paper, the atmospheric pollution observation network in this country is currently using the wet (chemical measurement) method in most cases. However, the adoption of the dry (physical measurement) method is being investigated.

References

1. Chubachi, S., "Preliminary Result of Ozone Observation at Showa Station From February 1982 to January 1983," Mem. Natl. Inst. Polar Res., Spec. Issue, No 34, 1984, pp 13-19.
2. Nakane, H., "Measurement of Ozone Layer by Laser Radar," OPTOELECTRONICS, No 5, 1989, pp 87-92.
3. Nakane, H., "Optical Technique for Exploring Ozone Layer-Related to Ozone Holes," OPTICS, No 18, 1989, pp 56-60, edited by "Ozone Layer Protection Study Group of the Environmental Agency, "Protecting the Ozone Layer," NHK Publishing Assoc., 1989.

4. Hasebe, F., "Observation of Stratospheric Ozone Layer by Meteorological Satellites--Trial With NIMBUS-4 BUV--," WEATHER, No 29, 1982, pp 29-57.
5. Kunugi, M., "Analysis of Trace Gas Components," ULSI, No 6, 1986, pp 22-32.

Chemical Sensor Using Polymer Film Electrodes

43067185c Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 53-55

[Article by Noboru Koyama, Tokyo University of Agriculture and Technology]

[Text] There has been tremendous advancement in analytical instruments for environmental and medical measurements as a result of progress in microelectronics, and they can now provide us with necessary information for carrying out scientific observation on environmental conditions that surround us or on medical conditions. The objects of materials to be detected are increasing in number, the total measuring system is becoming systematized, and the possibility of carrying out simple and quick measurements is being pursued. Among them, various electrically conductive materials are used as transducers or detectors to grasp such information as the concentration of materials to be detected. The development of such functional materials is also remarkable. When a conductive material is used by immersing it in a solution, it is generally called an electrode of an electrochemical system. An electrode which is modified by directly fixing a third material on the surface is called a chemically modified electrode. The development of chemically modified electrodes made it possible to add a new reactivity or selectivity to the existing functions of the electrode surface and to produce interfaces with high functions which can display a new functionality.

1. Sensing Function

A variety of functional thin films are currently in use as chemical modifiers for the electrode surface. The use of a thin film makes it possible to realize high density of a functional group to be introduced to the electrode surface or three-dimensional use of a new reaction field, so that it gives hope for enhanced selectivity of a reaction to a substrate and for enhanced durability of a fixed functional group. Table 1 shows sensor functions that can be realized by the use of a thin film. At present, surveys and monographs that describe the results of these studies are published in large number.

In general, electrochemical sensors can be classified from the principle of operation into 1) amperometric method which detects by the redox reaction the substance to be detected; 2) potentiometric method which detects a change in concentration as a change in equilibrium potential; and 3) a method for detecting the change in the surface charge in an insulating layer and on a

Table 1. Modified Surfaces and Functions

Interaction	Function manifested
Desorption	Stabilized potential or current response
Singular adsorption	Generation of a surface or film potential
Electrode catalyst	Generation of an amplified current by cycling redox reaction catalyst
Conversion to detectable substance	Equilibrium potential response due to concentration of converted substance or current response due to its redox reaction
Selective concentration	Large current response due to generation of film potential or redox reaction of converted substance
Selective permeation	Prevention of access of auxiliary reaction species to the electrode and selective current response or equilibrium potential response
Fixation/protection of specific substance	Maintenance of equilibrium potential or fixed potential for surface fixed species and species to be detected
Charge distribution change on electrode surface	Potential difference caused by electrolytic effect
Optical response	Generation of photocurrent or photovoltaic force due to optical excitation

semiconductor surface. Here, the features of the sensitive films in (3) can be applied directly to sensors based on the measuring method of (2), so that polymer film coating for electrode substrates is very useful for both cases. Work in this field will be presented in this paper centered around the research by this author and his colleagues.

2. Potential Response Element

It is possible to manufacture field-effect transistors (FETs) that respond selectively to various kinds of ions (H^+ , K^+ , Na^+ , Li^+ , NH_4^+ and Ca^{2+}) (called ISFETs) by connecting a minute carbon electrode with a diameter of 0.2 mm on the tip of the gate part of commercially available FETs and covering the surface with a two-layered polymer thin film.^{1,2} As shown in Figure 1, the inner film of such a two-layered film consists of a redox active electrolytically polymerized thin film (poly (1-pyrenamine, poly(p,p'-biphenol), poly(2,b-dimethylphenol), etc., of thickness of 1-10 μm),³⁻⁷ and the outer film consists of a neutral carrier (NC) film (with thickness of 300-1,000 μm). The NC film has a polyvinylchloride film as a matrix, contains ionophores for each ion (tri-n-dodecylamine (H^+), valinomycin (K^+), bis [(12-crown-4) methyl] dodecylmalonate (Na^+), bis [di-(n-octylphenyl)-phosphate] calcium (Ca^{2+}), monactin (NH_4^+), 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetradecane (Li^+)), and consists of a plastic material (diocytylsebacate or o-nitro-phenyloctylether), and potassium tetrakis (4-chlorophenyl) borate.

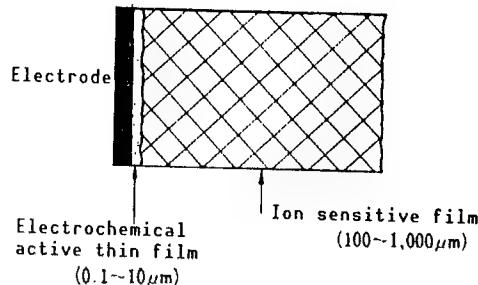


Figure 1. Diagram of Electrode Coated With Two-Layered Film (Ion sensitive film contains ionophores such as H^+ , K^+ , Na^+ , Li^+ , NH_4^+ , Ca^{2+} , etc.)

The inner film of an ISFET manufactured has the function corresponding to the internal reference electrode and the solution of a liquid film type ionic electrode, and the outer film has the function of the ion selectivity sensitive film. The activity range that shows the ion selectivity and the Nernst response are comparable to those of the ordinary liquid film type ionic electrode. In an electrode coated with an NC film alone, there are observed effects of dissolved oxygen and carbon dioxide, but in a two-layered coated electrode, these effects are not seen and has an excellent long-term stability (more than 4 months in the case of K^+ -ISFET, for example), and the potential drift is also small (0.2 mV/h for K^+ -ISFET, for example). Further, in a circulation experiment using the standard human serum and bovine blood plasma, continuous monitoring of longer than 1 day is possible, and the electrode performance will not be modified by sterilization in the autoclave (at 121°C for 20 minutes). Further, by incorporating a system for compensating for temperature change during the measurement in a measuring circuit, it is possible to trial manufacture a continuous monitoring system (Figure 2).

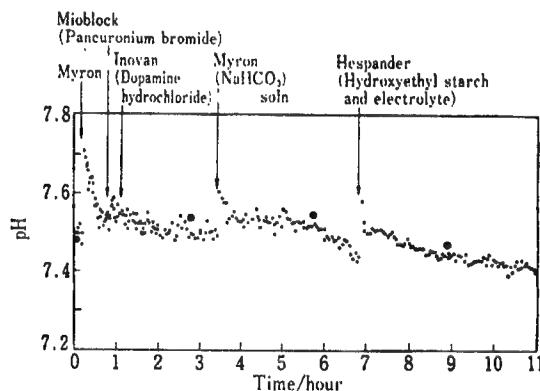


Figure 2. Continuous Monitoring (•) of pH Changes in Canine Blood of in vitro Circulation System
An arrow indicates injection of a carbonate (•) indicates a measured pH value using a blood gas meter commercially available.

3. Current Response Element

(1) Elements Using Permeation, Separation and Concentration Actions

A poly-cationic polymerized electrolytic thin film electrode having ionane structure manufactured in situ by electrolytic oxidation and polymerization of N,N-di-substituted aniline derivatives (N,N-dimethylaniline, etc.) has a selective concentration action to anion species, and amperometric determination of polyvalent anion redox species in the range of $10^{-10}\text{--}10^{-9}\text{M}$.⁸ Moreover, the electrochemically inactive poly(2,b-dimethyl-1,4-phenylene oxide) thin film obtained by electrolytic oxidation and polymerization of 2,b-dimethyl-phenol has a selective permeation/separation action that depends on the ionic radius to various redox ions. Ions with radius greater than about 3 Å cannot in reality permeate such a film, so that the thin film coated electrode can, for example, be expected as a pH sensor.⁹ In both cases, the electrode system is a fully solid type and can be miniaturized.

(2) Elements Using Electrode Catalytic Action

A two-layered film coated microelectrode having the structure of carbon electrode substrate/electrolytically polymerized poly (cobalt porphyrin) thin film (thickness of 1~10 μm)/glucose oxidase (GO) film (thickness of 10~100 μm) can be expected as an in vivo and in vitro glucose sensor.¹⁰ In this case, the glucose concentration is determined by measuring the amount of enzyme consumed in the enzyme reaction based on the catalytic action of the cobalt porphyrin film to the oxidation-reduction reaction by current measuring method (Figure 3). Further, an electrode consisting of carbon substrate/clay thin film (mediator: $\text{Ru}(\text{NH}_3)_6^{2+/3+}$)/GO_x film functions as a glucose sensor based on the catalytic reaction of the clay thin film for the reduction reaction of H_2O_2 generated in the enzyme reaction (Figure 4).¹¹

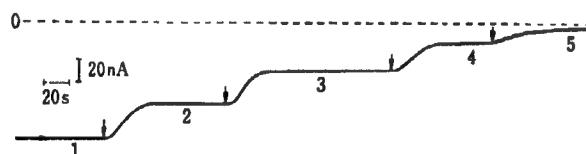


Figure 3. Output Current Response of Two-Layered Type Film Coated Electrode to Injection of Glucose (Oxygen reduction measured at -0.55 V (against saturated calomel electrode))

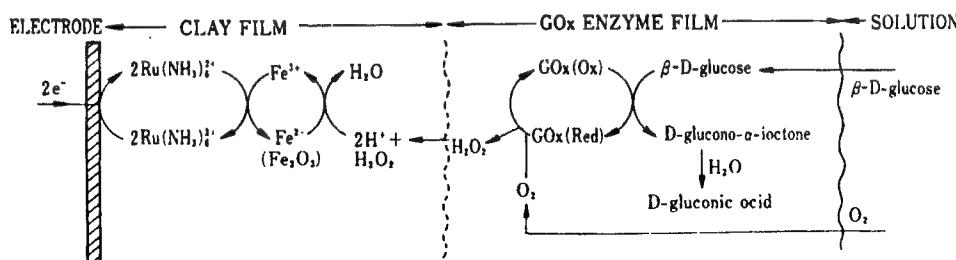


Figure 4. Principle of Operation of Coated Electrode Consisting of Clay Film and Enzyme Film Acting as Glucose Sensor

A large number of mediation reactions for enzymes using ferrocene derivatives or metallic complexes are known. Lowe, et al., electrolytically polymerized pyrrole monomer modified by ferrocene with a solution containing glucose oxidase, and reported on the behavior of the thin film coated electrode obtained in this reaction.¹² A cyclic voltamogram in an electrode coated with poly(ferrocenylamide propylpyrrole/pyrrole) copolymerized body including glucose oxidase gives an irreversible oxidation response that depends on the glucose concentration, and suggested catalytic oxidation of glucose oxidase accompanying oxidation and reduction of a ferrocenyl site and possibility as a glucose sensor. On the other hand, Heller, et al., reported that they were able to realize electron migration to the enzyme activation centers on the electrode by modifying flavin-based enzymes (glucose oxidase and D-amino acid oxidase) with ferrocene derivatives, Ru complexes, etc.^{13,14} Each of the chemical modifier enzymes showed an increase in the oxidation current for an increase in the substrate concentration. Further, they made catalytic oxidation reaction of glucose oxidase possible by the use of cationic polymerized complexes.¹⁵ A poly(N-methylvinylpyridinium chloride)/poly(vinyl-pyridine O₅(bPy)₂Cl) copolymer modified electrode that fixed glucose oxidase electrostatically showed an irreversible oxidation reaction in the coexistence of glucose, so that the development of an enzyme sensor using this hybrid enzyme is expected.

4. New Reference Electrode

As a new reference electrode, a polyimide film (thickness of 2-50 μm)/electrolytically polymerized film (thickness of 1-25 μm) FET reference electrode was manufactured based on a principle similar to that of ISFET. It was found that this FET reference electrode does not respond to pH in the range of 2-10, no effect of dissolved oxygen or carbon dioxide is observed and that the potential drift is small (0.2 mV/h). This electrode responds to the ion intensity (particularly that of negative ions) in the solution, and may be used as an ion sensor. However, in a solution containing a certain concentration of electrolytic ions, such as sodium chloride in blood, the electrode is independent of the concentration change of other ions so that it was found that it is suited as a reference electrode of a sensor system based on ISFET.¹⁶

The central task of the research on modified electrodes is to design and control the electrode surface on the level of molecules by use of a third chemical substance, and it is very interesting in its relation with the reaction system of living bodies. Interesting reports up to the mid-1980's are compiled in a monograph.¹⁷ However, in order to try to put the modified electrodes to practical use as detectors for analysis, several difficult tasks have to be overcome. First, even when the third substance fixed to the electrode surface interacts specifically with the substrate to manifest a new function, the fixed species has to satisfy the condition that it is insensitive to the interaction with other dissolved chemical species. Further, the fixed species itself has to be extremely stable on the electrode surface and a specific interaction has to be maintained stably. Eventually, the response speed must be high and the measurement accuracy must also be high. Some of the examples reported in the present paper are expected to be applied to new detection elements of liquid chromatography.

References

1. Oyama, N., Hirokawa, T., Yamaguchi, S., Ushizawa, N. and Shimomura, T., ANAL. CHEM., Vol 59, 1987, p 258.
2. Oyama, N., Ohsaka, T., Yosimura, F., Mizumuna, H., Yamaguchi, S., Ushizawa, N. and Shimomura, T., J. MACROMO. SCI. CHEM., in press.
3. Oyama, N., Ohsaka, T., Ohnuki Y. and Suzuki, T., J. ELECTROCHEM. SOC., Vol 134, 1987, p 3068.
4. Chiba, K., Ohsaka, T., Ohnuki, Y. and Oyama, N., J. ELECTROANAL. CHEM., No 219, 1987, p 117.
5. Osaka, T., Yoshimura, F., Hirokawa, T. and Oyama, N., J. POLYM. SCI. PART C, POLYM. LETT., Vol 25, 1987, p 395.
6. Oyama, N., Ohsaka, T., Hirokawa, T. and Suzuki, T., J. CHEM. SOC., CHEM. COMMUN., 1987, p 1133.
7. Katsume and Koyama, SENSOR TECHNOLOGY, Vol 8, 1988, p 47.
8. Ohsaka, T., Okajima, T. and Oyama, N., J. ELECTROANAL. CHEM., Vol 200, 1987, p 159.
9. Ohsaka, T., Hirokawa, T., Miyamoto, H. and Oyama, N., ANAL. CHEM., Vol 59, 1987, p 1758.
10. Ohsaka, N., Kobayashi, M., Ohsaka, T. and Mizumuma, M., Ibid., Vol 61, 1988, p 2534.
11. Oyama, N. and Ohsaka, T., manuscript in preparation.
12. Foulds, N.C. and Lowe, C.R., Ibid., Vol 60, 1988, p 2473.
13. Degani, Y. and Heller, A., J. PHYS. CHEM., Vol 91, 1987, p 1285.
14. Ibid., J. AM. CHEM. SOC., Vol 110, 1988, p 2615.
15. Ibid., Vol 111, 2357, 1989.
16. Ohyama, N., Ohsaka, T., Ikeda, S. and Okuaki, K., ANAL. SCI., submitted.
17. Senda, Aizawa and Koyama, editors, POLYMERIC FUNCTIONAL ELECTRODES, Academic Publication Center, 1983.

Wet Optical Sensor

43067185d Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 56-58

[Article by Masao Kaneko, Institute of Physico-Chemical Research]

[Text] An optical sensor detects optical information by converting it to signals such as electrical ones. For this purpose it is usual to carry out photoelectric conversion by a semiconductor solid-state element. Since such photoelectric conversion function is manifested only when the semiconductor is put to p-n junction type or Schottky junction type by bringing the semiconductor into contact with a metal, it is not an easy task to obtain an element for the above purpose. In contrast, barriers formed by the interfaces of semiconductors and electrolytic solutions have become the subject of interest in recent years. These are a type of Schottky type barrier, called liquid junctions in particular, and have photoelectric conversion function. Such a junction can be formed by simply immersing a semiconductor in an electrolytic solution so that an element can be realized in an astonishingly simple way. Moreover, electric charges generated on the surface of the semiconductor can oxidize or reduce redox species in the solution, and hence it is possible to output a photocurrent and reaction products in the form of chemical energies. In other words, a wet optical sensor can function not only as a photocurrent response sensor but also as a photochemical response sensor which should also be applicable to the detection and analysis of chemical substances. Organic polymeric semiconductor materials can also be made into wet sensors in a simple manner, and they can manifest the functions described above.^{1,2}

In a wet system, electron migration from an optically excited state takes place easily so that it is possible to construct a photochemical battery by utilizing this property. In addition, it can manifest not only a photoelectric response but also such new functions as photochemical response, which makes such sensors worth watching regarding future technology whose nucleus will be photonics.

In this paper, works of this author centered around the photophysico-chemical elements that utilize polymer semiconductor materials and photochemical elements that utilize polymer films will be presented.

1. Polymer Semiconductor Element

When a semiconductor is immersed in an electrolytic solution, a Schottky type barrier is formed (Figure 1). Because of this so-called liquid junction the semiconductor manifests the photoelectric response function. Moreover, the holes (in the case of n-type) or the electrons (in the case of p-type) that migrate to the semiconductor surface under irradiation of light can oxidize or reduce compounds in the solution. It was found that similar to the inorganic semiconductors the polymer semiconductors can constitute liquid junction type elements. In addition to semiconductors such as polythienylene³(1), polyaniline⁴(2) and polypyrrole^{5,6}(3) that are obtained as thin films by electrolytic oxidation and polymerization, a polyacetylene (4) film⁷ manifests the photoelectric response function by a simple immersion in an electrolytic solution. The photocurrent induced in a polythienylene film by the three-electrode system when voltage is applied is shown in Figure 2.³ The photocurrent generated in this case is reversibly stable.

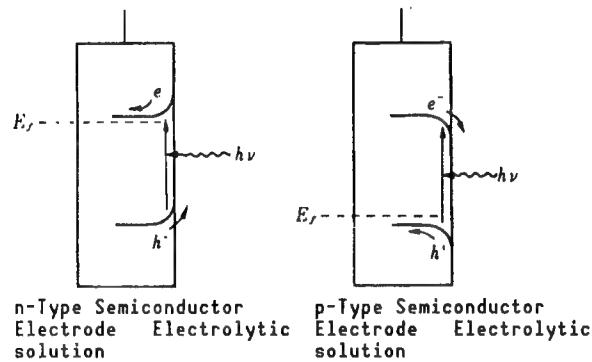
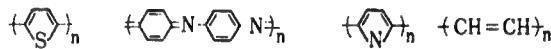


Figure 1. Formation of Schottky Type Barrier at the Interface of Semiconductor/Electrolytic Solution (Ef: Fermi level)

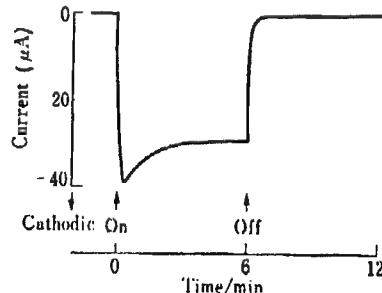
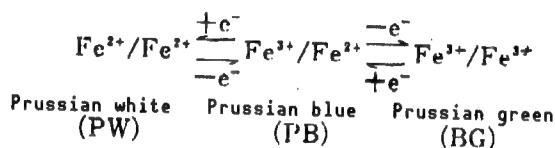


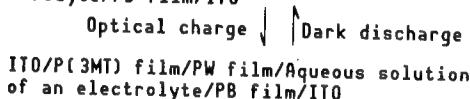
Figure 2. Photocurrent Induced by a Polythiophylene Film (1.8 cm^2) Immersion in an Electrolytic Solution (0.1 M LiClO_4) (Electrode potential -0.2 V vs. $\text{Ag}-\text{AgCl}$)

By utilizing the redox reactions on the interface of a liquid junction type element, it is possible to construct an optical charge storing element which accumulates electric charges that are isolated under the irradiation of light, and provides a current when needed by discharging.⁸ As a polymer raw material that is capable of storing both positive and negative charges, Prussian blue (PB) was selected. PB is a mixed valence complex consisting of cyano complexes of divalent and trivalent iron, and is a polymer with molecular weight of about 7 million having a chain of a large repetition structure ($Fe^{3+}[Fe^{II}(CN)_6]^{4-}$). It can readily be put in the form of a film by an electrolytic method. Based on reversible two-stage redox reactions (Scheme 1) of iron ions, both positive and negative charges can be stored so that it is possible to construct a secondary battery with sheets of PB films.⁹

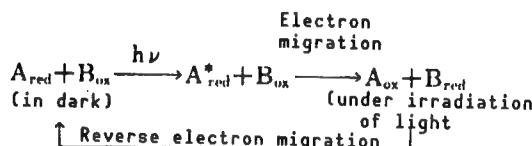


Scheme 1

ITO (electrically conductive glass electrode)/
P(3MT) film/PB film/Aqueous solution of an
electrolyte/PB film/ITO



Scheme 2



Scheme 3

By combining the PB film secondary battery with a photoelectric response element an optical charge storing element is obtained. For example, by coating the surface of a poly(3-methylthiophene) (P3MT) film, and using a bare PB film as a counter electrode, it is possible as shown in Scheme 2 to accumulate electrical charges under the irradiation of light and release the charge when the element is in the dark.¹⁰ This situation is illustrated in Figure 3.

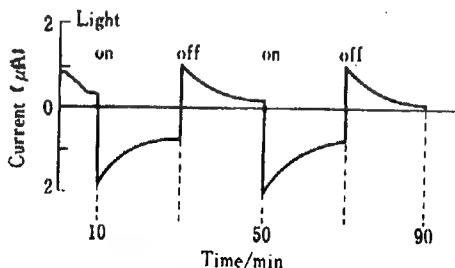


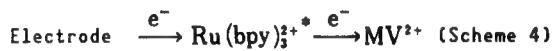
Figure 3. Optically Charged Current Induced by Scheme 3 and Discharge Current in Dark

In addition, oxidation and reduction of various compounds can be performed under the irradiation of light so that it is possible to design a photochemical conversion system which can take out light by converting it in the form of a chemical substance.

2. Photochemical Sensor

By the use of photochemical reactions it is possible to manufacture photoelectric response elements without using semiconductors.¹¹ This is also called a photogalvanic cell. If the equilibrium of the photochemical reaction leans toward the generating system under the irradiation of light (Scheme 3), it is possible to easily obtain a photocurrent by irradiating the surroundings of only one of the two electrodes immersed in the solution and keeping the other in the dark.

If the reverse electron migration is fast and the equilibrium does not lean toward the generating system even under the irradiation of light, a photocell cannot be constructed easily. However, it is known that a photoelectric response can be obtained by coating one or both of the reaction components in the form of an electrode coated with a polymer film.^{12,13} For example, electron migration from an optically excited state of tris(2,2'-bipyridine) ruthenium (II) complex ($Ru(bpy)_3^{2+}$) to methylviologen (MV^{2+}) has a fast reverse reaction so that a photoelectric response cannot be obtained under normal conditions. However, by forming a two-layered polymer film on each of the electrodes, a photoelectric response can be generated under the application of voltage¹² (Scheme 4).



Since PB described in the previous section has an action as an electron acceptor the electrode/polymer $Ru(bpy)_3^{2+}$ film/PB film system also has the photoelectric response function. Its potential diagram is shown in Figure 4.¹³

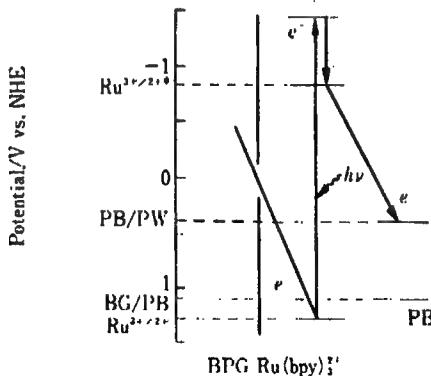
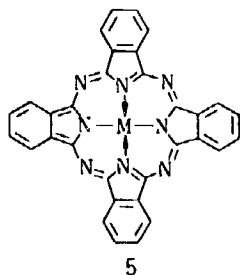


Figure 4. Mechanism of Photocurrent Induced by Electrode/Polymer $Ru(bpy)_3^{2+}$ Film/PB Film in the Aqueous Solution of an Electrolyte



Further, an electrode coated with a metallic phthalocyanine (5) is immersed in the aqueous solution of an electrolyte, a photoelectric response cannot be generated in the absence of oxygen even when it is irradiated with light. However, when oxygen coexists, the system becomes an electron acceptor so that a photoelectric response is generated in proportion to the concentration of oxygen¹⁴ (Scheme 5).

ITO/Film dispersed with phthalocyanine polymer $\frac{h\nu}{e^-} O_2$
(Scheme 5)

Such a photochemical cell will become applicable to analysis and determination of chemical substances by the use of light.

3. Future Development

For wet sensors, various raw materials can be used since it is easy for them to be put to elements and develop into nonconventional sensors such as photochemical sensors. This is a field in which basic research and development and application in the future hold great hopes.

References

1. Kanebo, M., "Functional Organic Thin Films (Outline of Chemistry Series No 45)," Academic Societies' Publication Center, 1984, p 183.
2. Ibid., POLYMER PROCESSING, Vol 35, 1986, p 25.
3. Kenmochi, T., Tsuchida, E., Kaneko, M. and Yamada, A., ELECTROCHIM. ACTA, Vol 30, 1985, p 1405.
4. Kaneko, M. and Nakamura, H., J. CHEM. SOC., Chem. Commun., 1985, p 346.
5. Inoue, T. and Yamase, T., BULL. CHEM. SOC. JPN., Vol 56, 1983, p 985.
6. Kaneko, M., Okuzumi, K. and Yamada, A., J. ELECTROANAL. CHEM., Vol 183, 1985, p 407.
7. Yamase, T., Harada, H., Ikawa, T., Ikeda, S. and Shirakawa, H., BULL. CHEM. SOC. JPN., Vol 54, 1981, p 2817.
8. Kaneko, M., ELECTRONICS, Vol 10, 1984, p 97.

9. Kaneko, M. and Okada, T., J. ELECTROANAL. CHEM., Vol 255, 1988, p 45.
10. Kaneko, M., Takahashi, T. and Tsuchida, E., J. ELECTROANAL. CHEM., Vol 227, 1987, p 255.
11. Kaneko, M. and Wöhrle, ADV. POLYM. SCI., Vol 84, 1987, p 141.
12. Kaneko, M., Moriya, S., Yamada, A., Yamamoto, H. and Oyama, N., ELECTROCHIM. ACTA, Vol 29, 1984, p 115.
13. Kaneko, M., J. MACROMOL. SCI.-CHEM., Vol A24, 1987, p 357.
14. Kaneko, M., Wöhrle, D., Shlettwein, D. and Schmidt, V., MAKROMOL. CHEM., Vol 189, 1988, p 2419.

Organic Nonlinear Optical Materials

43067185e Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 59-61

[Article by Masasuke Umegaki, Tokyo Engineering University]

[Text] Along with the development and progress of semiconductor lasers, lasers that have so far been utilized only for scientific purposes are now actively applied to devices and systems familiar in general society. Because of the excellent spatial and temporal coherencies, different from those of an ordinary light source, laser beams have features of high density and parallel processability with respect to spatial properties, fast responsiveness with respect to temporal properties, and diversity in wavelength and frequency. That these features are widely utilized in optical sensing technology is a well-known fact.

On the other hand, as a result of combining these features, the laser beam itself has an extremely high intensity electric field of light that cannot be obtained by an ordinary light source. When a very high intensity electric field of light exists, nonlinear optical effect generated by electric polarizations that are proportional to the square and the cube of the field intensity induced in a substance becomes conspicuous. In order for the laser, in particular the semiconductor laser, to be applied in the future to diversified fields, there must be various kinds of control on the laser. For the control of light, the nonlinear optical effect, especially the second order nonlinear optical effect is utilized in some form.

In this paper, various kinds of optical functional elements that make use of nonlinear optical effects and organic nonlinear optical materials that are being more actively studied and developed in recent years will be described.

1. Wavelength Conversion Element

The nonlinear polarization of a material can be represented in terms of the electric field of light E_j as in the following equation:

$$P_{1(2)} = \epsilon_0 X_{ijk}^{(2)} E_j E_k$$

$$P_1^{(3)} = \epsilon_0 X_{ijkl}^{(3)} E_j E_k E_l$$

In the above equations, ϵ_0 is the dielectric constant in vacuum, $X_{ijk}^{(2)}$ and $X_{ijkl}^{(3)}$ are nonlinear electric susceptibilities, and i, j, k, l and x, y, z are coordinate axes within a crystal.

$P^{(2)}$ and $P^{(3)}$ are called the second order and the third order nonlinear polarizations. Elements that convert wavelength of laser beam that utilizes the second order nonlinear polarization will be described in the following.

When optical electric fields with angular frequencies ω_1 and ω_2 exist simultaneously on a material, nonlinear polarized waves, $P^{(2)}$, with angular frequencies $\omega_1 \pm \omega_2$ are induced within the material. Then, the sum and difference frequency waves with the angular frequencies $\omega_1 \pm \omega_2$ and coherence equivalent to that of the laser are generated. The generation of the sum frequency in the case of $\omega_1 = \omega_2 = \omega$ is called the generation of the optical second harmonic wave with a frequency twice as large and a wavelength half the fundamental laser beam, and it is the method of wavelength conversion that is most widely in use. The conversion efficiency of this process is larger for higher intensity of the fundamental beam. Further, in order to realize wavelength conversion with high efficiency, it is necessary to carry out phase matching which brings the phase velocities of the nonlinear polarized wave and a new optical wave generated by it.

While limitations to the development of lasers with short oscillation wavelength that utilize II-III semiconductors are seen, generation of a coherent beam in the range of green to blue is about to be achieved by highly efficient wavelength conversion of semiconductor lasers in the near infrared wavelength region.

As one such method, a device is under development which carries out a high efficiency conversion by the use of high intensity of the fundamental wave within a resonator obtained by arranging a nonlinear optical crystal in the resonator for small-size Nd:YAG laser for semiconductor laser excitation.¹

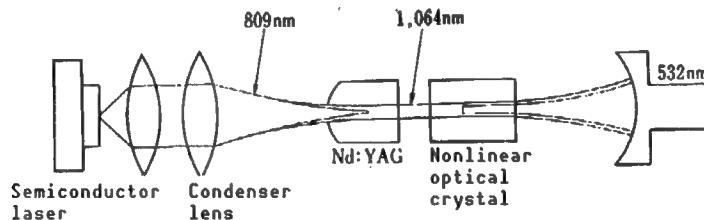


Figure 1. Generation of Second Harmonic Optical Wave Within YAG Laser Resonator Excited by Semiconductor Laser

Figure 1 shows this element. A second harmonic optical wave of 532 nm (about 10 mW) is obtained with YAG laser with oscillation wavelength of 1,064 nm excited by a semiconductor laser array (200 Mw) with wavelength of 890 nm. Further, it is possible to obtain a second harmonic with 473 nm by oscillating a laser with wavelength of 946 nm, or to obtain a coherent light of 459 nm by generating a light with sum frequency from 809 nm and 1,064 nm light waves. For the nonlinear optical crystal inorganic materials such as KNbO_3 and KTiOPO_4 are used. However, the size of the element is fairly large so that the range of practical use is limited accordingly.

Another possible method is the direct conversion of the fundamental wave laser which uses optical fibers or channel type optical waveguide, contains the fundamental wave in a narrow space of the order of several micrometers, and utilizes the augmented optical intensity. An optical waveguide is not just a condenser but a device which makes it possible to propagate light in the contained state for a long distance.²

Figure 2 shows a second harmonic optical wave generating element of a semiconductor laser which uses a proton exchange $\text{LN}(\text{LiNbO}_3)$ channel type waveguide.³ Using a phase matching method called Cerenkov radiation 1 mW blue light from a 50 mW fundamental wave is obtained. An element by a similar system is also being tried using an optical fiber that has an organic nonlinear optical crystal as the core.

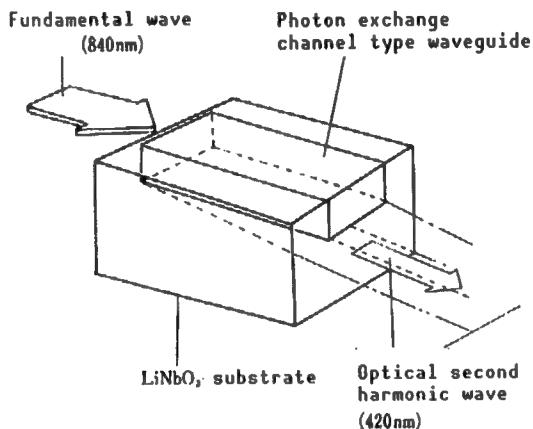


Figure 2. Optical Second Harmonic Generation by Proton Exchange LiNbO_3 Channel Type Waveguide

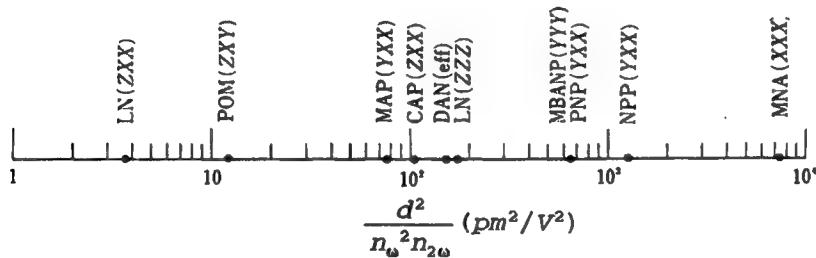


Figure 3. Performance Index of Various Kinds of Organic Materials
(Symbol in parentheses is the component of nonlinear optical constant)

The intensity of the second harmonic optical wave is proportional to $d^2/n_\omega^2 n_{2\omega}$, where n_ω and $n_{2\omega}$ are indices of refraction for waves with frequencies ω and 2ω , respectively, and d is given by $d = X^{(2)}/Z$. The second order nonlinear optical performance index for various organic materials is shown in Figure 3 in comparison with that of LN that has a high performance among inorganic materials. It will be seen that the organic materials have an extremely high performance compared with the constant d_{ZXX} for which phase matching becomes

possible by the use of double refraction of a bulk crystal, and the constant d_{zzz} for which phase matching becomes possible only after making it into a waveguide.⁴ Basically, as in the case of paranitroaniline p-NA shown in Figure 4, when an electron donative group and an electron attracting group (amino group and nitro group) are given to the π electron reservoir (benzene ring in the case of p-NA), intramolecular charge migration takes place for the existing optical electric field, manifesting large nonlinearity. Development of organic nonlinear optical materials with very high performance will continue actively into the future.



Figure 4. p-NA Molecule

2. Optical Modulation Element

Development of a waveguide modulation element which utilizes the first order electrooptic effect of LN as a modulation element for a semiconductor laser is still being pursued actively at present. The first order electrooptic effect which causes the index of refraction to be changed by the application of an electric field can be represented by

$$\begin{aligned} D_i &= \epsilon_0 n^2 D_j \omega \\ &= \epsilon_0 (1 + X_{ij}^{(1)} + S_{ijk(2)} E_j) E_i \omega \end{aligned}$$

where $E_i \omega$ is the electric field of the light, E_j is the applied electric field, D_i is the electric displacement and n is the index of refraction. Therefore, it will be seen that the organic materials shown in Figure 3 will surely display large electrooptic effect.

Attracting attention is an interesting topic in the field of developing materials aimed at utilizing the nonlinearity on the molecular level of organic materials that do not readily lend themselves to bulk crystallization is that of field oriented polymers which is illustrated in Figure 5. Guest molecules manifesting nonlinearity in the second order is dispersed in a polymer film or made in the form of a copolymerized film. Then, the second order nonlinearity is macroscopically generated by orienting the molecules through application of an electric field. An interesting aspect is that the index of refraction for polarized light in the direction of orientation at the portion of orientation becomes large, so that a channel type optical waveguide is formed as shown in the figure. As a result, a waveguide modulation element analogous to LN can be found. Materials with electrooptic coefficient exceeding that of LN have already been developed. Although there still remain the change with time of orientation, dilution of concentration of guest molecules and other matters as unsolved problems, future advancement in this field is expected.

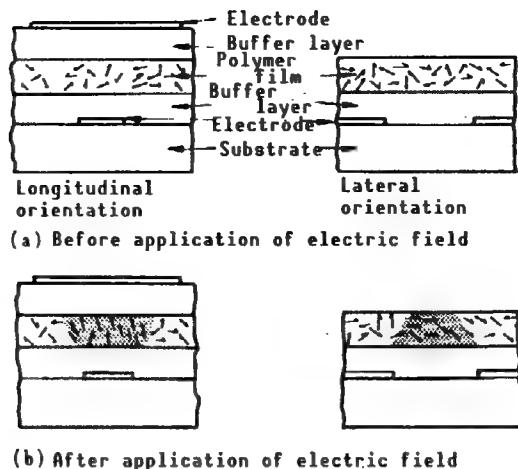


Figure 5. Method of Orienting Guest Molecules in Polymer Film and Formation of Channel Type Waveguide

If sources of visible coherent light by wavelength conversion of semiconductor lasers are developed, then the development of various kinds of devices as small-sized and handy light sources for measuring optical interference, holography and other things will be pushed further. Furthermore, flexible filmlike electrooptic elements will undoubtedly find their way not only as waveguide modulation elements but also as voltage change detection elements. Expectation for organic nonlinear optical materials is high.⁵

References

1. Lin, J.T., et al., "Choosing a Nonlinear Crystal," LASERS & OPTONICS, Vol 6, 1987, p 59.
2. Informal Discussion Group on Optics, Applied Physics Society of Japan, ed.: "Optical Integrated Circuits," Asakura Book Store (1987).
3. Taniuchi, "Optical Nonlinear Waveguide and Harmonic Wave Generation," OPTICS, Vol 16, 1987, p 254.
4. Umegaki, "Generation of Second Optical Harmonic Using Organic Materials," Ibid., Vol 18, 1989, p 309.
5. Chemla, D.S., et al., "Nonlinear Optical Properties of Organic Molecules and Crystals," Academic Press, 1987.

Pressure Sensitive Conductive Rubber

43067185f Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 62-67

[Article by Koichi Kawashima, Yokohama Rubber Co.]

[Text] Among composite type conductive polymeric materials which are a mixed dispersion of electrically conductive powder and an insulating polymeric material, the first one to be developed into a practical material was conductive rubber. Since conductive rubber has properties different from other conductive materials, such as metals, it caught the interest of many workers, and has been examined extensively from both theory and application. However, only a few materials of this kind have been pushed to the state of practical materials.

Later, the use of synthetic rubber became widespread and the industrial importance of carbon black that is added to enhance the mechanical performance of rubber products has been increased significantly. Because of the shift in the manufacturing method from the conventional channel black to furnace black in order to improve the reinforcing and to meet the increase in demand, the structure of carbon black (secondary particle structure which is an aggregate of lumps formed by primary particles that are assemblies of small graphite crystals) has been developed. In addition, a large amount of carbon black is mixed so that among various rubber products of today it is not uncommon to see a specific volume resistance smaller than $1 \Omega \cdot m$.

1. Conductive Rubber

In the initial stage of development for application of conductive rubber, there was little accomplishment outside the field of electrostatics (destatization) where an effect can be expected at specific resistance of about $10^3 \Omega \cdot m$ for which manufacture is easy. This is due to the fact that the resistance of conductive rubber is extremely unstable. For example, reproducibility in manufacturing is almost nonexistent and the resistance of the product changes easily by a change in temperature and deformation due to external force.¹

The only exception to the above is a switch contact made of silicone rubber that is rendered conductive by the use of carbon black. This is used as a switch for a semiconductor circuit, and the resistance is high at the time of closing the circuit, or even when the resistance has a dispersion in its

value, it only needs to be able to discriminate closing the circuit from opening. Therefore, it can be said that this is a use in which the drawbacks of conductive rubber are of little concern.

This material can readily be obtained by mixing acetylene black or furnace black of conductive grade (ketjen black is famous) to silicone rubber polymer, and crosslinking using an organic peroxide (dicumyl peroxide in most cases). All of the makers of silicone material are selling a material of this kind in blended form, so that the rubber processor need only purchase the material and process it by mixing according to the treatment method recommended by the material maker.

2. Pressure Sensitive Conductive Rubber

Pressure sensitive conductive rubber utilizes the fact that the resistance of a composite conductive rubber changes under an external force. Electric current in conductive rubber flows through a chain of conductive particles that are in contact or adjacent to each other (Figure 1). Regarding the formation of the chains, many theoretical analyses have been done, and lately it is said that the percolation theory² is considered most favorably. When the material of the dispersed system generates a distortion due to external forces, the mutual configurations of the conductive particles are changed which bring about changes in the conductivity. That these changes are great when the particles have independent shapes without secondary structure can be easily inferred.

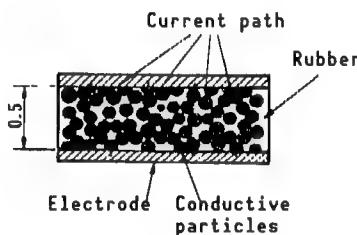


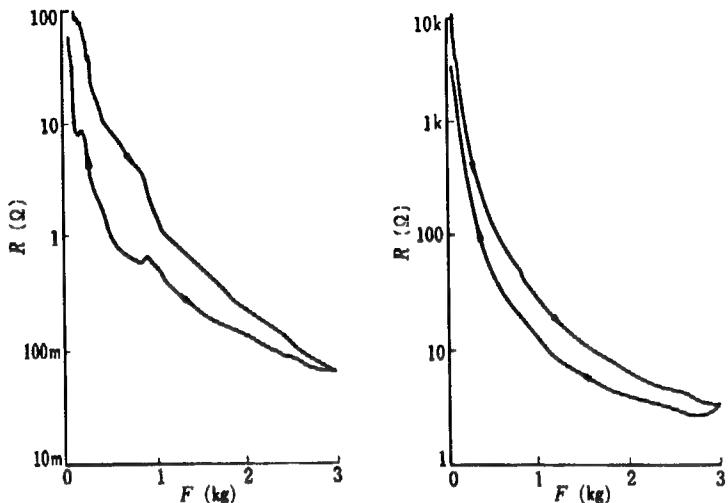
Figure 1. Current Path in Conductive Rubber

Pressure sensitive conductive rubber can be classified into digital and analog types from the viewpoint of practical use. The digital type rubber exhibits the so-called on-off changes which display insulating property when there is no external force and shows conductivity under an external force. Therefore, the digital type rubber acts as contactless switches characterized in the smallness of the stroke and the absence of a gap, so that they are put to practical use as tapelike or large-area touch switches.

In contrast, the analog type rubber produces continuous resistance in response to the magnitude of the external force, actually to the magnitude of the distortion generated, having a sensorlike function. Actual examples of this type will be presented in the following.

These two types are essentially the same, and the difference is merely in the level at which the resistance changes (Figure 2).³ A digital type material uses a metal as the conductive particles and the resistance in the low

resistance state is below 100Ω so that "among semiconductor circuits" it can be regarded as conducting. On the other hand, an analog type rubber uses high resistance particles such as carbon, and resistance change occurs in the range of $100 \text{ k}\Omega$ and 10Ω so that "among semiconductor circuits" it acts as a significant variable resistor.



Example of characteristic of a pressure sensitive conductive rubber using nickel particles (characteristic in the thickness direction, thickness of the sheet: 1 mm, shape of pressurized part: 8 x 8 mm)

Example of characteristic of a pressure sensitive conductive rubber using graphite particles (characteristic in the thickness direction, thickness of the sheet: 0.5 mm, shape of pressurized part: 8 x 8 mm)

Figure 2. F-R Characteristic of Pressure Sensitive Conductive Rubber
(Left: Digital type; Right: Analog type)

3. Analog Pressure Sensitive Conductive Rubber

A brief description of analog pressure sensitive conductive rubber and examples will be presented in the following.

The CS series (CS57-7RSC, CSA, etc.) manufactured by our company uses silicone rubber as the base and particles of synthetic graphite specially developed are blended in. They are now put to practical uses as a keying force sensor in electronic musical instruments and the material of the contact point for variable speed switches of an electrically operated zoom of a cam corder. The fundamental performance required of a pressure sensitive conductive rubber is the F-R characteristic (relationship between the pressurizing force and the resistance value), and this characteristic is mostly determined by the conductive filler used. Further, a necessary condition for practical use is the fact that change in the F-R characteristic that repeatedly withstands applied force (and resulting distortion) is small, where the nature of the conductive filler strongly affects the life of this property.

(1) Conductive Filler of CS

The pressure sensitive conductive rubber CS series has a particular feature in the conductive filler particles.⁴ By crushing a large lump as randomly as possible in the growth of small crystals of artificial graphite, then by making them round by removing corners of the particles by polishing, particles which look something like potatoes and which are used as the filler result (Photo 1). The size of the particles differs depending upon the use, but for the manufacture of a sheet with thickness specification of 0.5 mm, it is in the range of 150 to 325 mesh (for reference, particles of nickel pellet powder which is the metallic powder frequently used for digital type pressure sensitive conductive rubber are shown in Photo 2, and spherical particles obtained as graphite by baking liquid droplets of a polymeric material are shown in Photo 3).

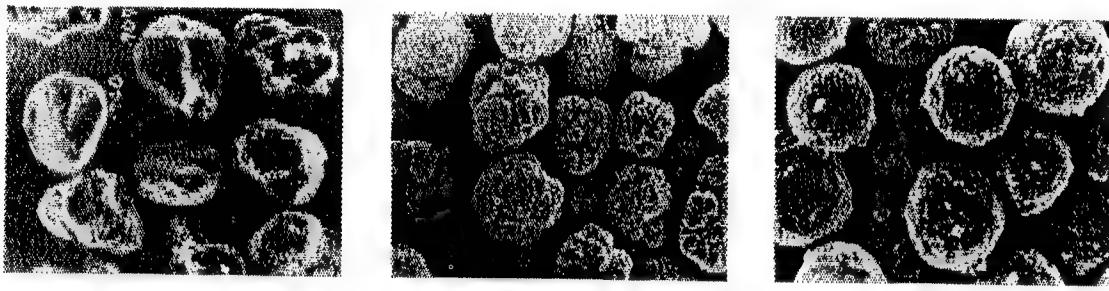


Photo 1

Photo 2

Photo 3

The fact that the material is graphite reduces the friction that is generated between particles at the time of a change in distortion, so that it contributes to the durability. In addition, perhaps due to appropriate softness, no noise (appearance of random spikelike variations in the F-R curve, without being smooth) is generated during distortion change observed in the case of metallic particles with similar shape. The roundness of particles is also an important factor in durability, and a roundness greater than 0.6 is necessary for durability that can withstand practical use. However, it has been observed that graphite particles closely shaped to a true sphere tend to produce a noise, contrary to our expectation, and it seems it is necessary that particles bite with each other somewhat during the change in distortion to deter an excessive mutual slipping.

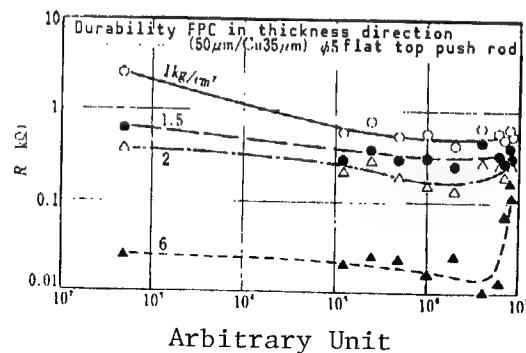


Figure 3. Durability Characteristic of CS Series

As a result of these provisions, the CS series pressure sensitive conductive rubbers was made to withstand several million to 10 million continuous, uninterrupted, repetitive loading tests with a peak load of 14 kg/cm^2 . At this point, for the first time, the pressure sensitive conductive rubbers had a level of durability for practical use (Figure 3).⁵

(2) Use of Pressure Sensitive Conductive Rubber

The first conceivable use of this kind of material has been force sensors. However, a pressure sensitive conductive rubber shows large hysteresis in the F-R characteristic or a creep phenomenon in which the resistance decreases with the lapse in time under a predetermined load so that it is extremely difficult to obtain a practical level for use as a sensor. Because of this, it has just begun to be put to practical use with special modification.

On the other hand, in the field of man-machine interface of electronic equipment, the use of examples known as a touch control switch (TCS) has spread. As can be seen from examples given below, feedback involving human interaction within the system is established, so that the problems in the characteristics of pressure sensitive conductive rubbers have been alleviated to some extent.

a. Touch Control Switch

(i) Keying force sensor

The keying force sensor is for controlling the after-touch of the electronic keyboard of a musical instrument (after-touch means to control a tone already output by hitting a key with a force applied to the keyboard). The trend for electronically wiring musical instruments is remarkable, and in particular among keyboard instruments an electronic organ represented by Electone (trademark of Yamaha Co.), and a synthesizer is a natural electronic musical instrument. For these keyboards it is obviously desirable to have the touch control function in which a strong sound can be output if pressed forcefully and a weak sound is output if pressed softly, rather than to have a mere array of pushbuttons. This is an area in which the pressure sensitive conductive rubber can show its usefulness.

The keying force sensor that has been put to practical use has a simple construction in which a ribbon of pressure sensitive conductive rubber placed between two sheets of metallic foil electrodes is accommodated in a channel obtained by profile extrusion of PVC, and covering it with felt. A body thus obtained is pasted in place of the conventional stopper felt (Figure 4). A resistor of 150Ω is connected in parallel with the sensor and, by supplying a constant current to it, the voltage across the terminals is taken out as a signal.

(ii) Zoom switch

The zoom switch is a variable speed electrically driven zoom TCS for a video camera with a built-in reproducing device. Zooming can be a method of expression since a video is a moving picture, and the zoom for a camera for

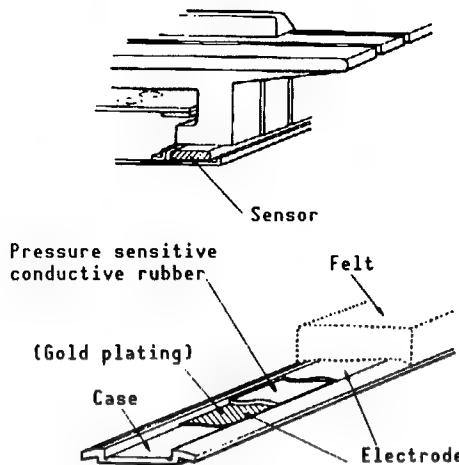


Figure 4. Keying Force Sensor for After-Touch

the professional has variable speed. The existing cam corder for the general public, however, uses an on/off switch due to cost considerations and restriction on space, and only zoom switches with fixed speed were available. However, with the use of pressure sensitive conductive rubber, it becomes possible to obtain a signal corresponding to the pressing force by the mere replacement of the contact material for the conductive rubber contact switch which has been used conventionally. In this manner, it is possible to obtain an electrically driven zoom switch variable speed within the same space as for the conventional on/off switch.

b. Sensor for Measurement

(i) TCS-5000 Series

The TCS-5000 is a sensor for detecting force and strain that uses pressure sensitive conductive rubber. The change in the resistance of a pressure sensitive conductive rubber is caused by a distortion generated in itself due to external force, and hence should more properly be called "distortion sensitive conductive rubber." The viscoelasticity of a pressure sensitive conductive rubber consists of a viscosity term characteristic to a rubber material and a friction term between conductive particles and between particles and rubber. Because of this, the relationship between external force and disturbance becomes nonlinear the result of which is reflected in the F-R characteristic. In fact, in the distortion-resistance characteristic of CS, the nonlinear elements such as hysteresis and creep are small (in comparison to the F-R characteristic) (Figure 5).⁶

A simple representation by a model of the above-mentioned property is shown in Figure 6. What can be inferred from the above is that the nonlinearity can apparently be improved by increasing the strength of the spring element (k). A realization of this idea is the 5000 Series.

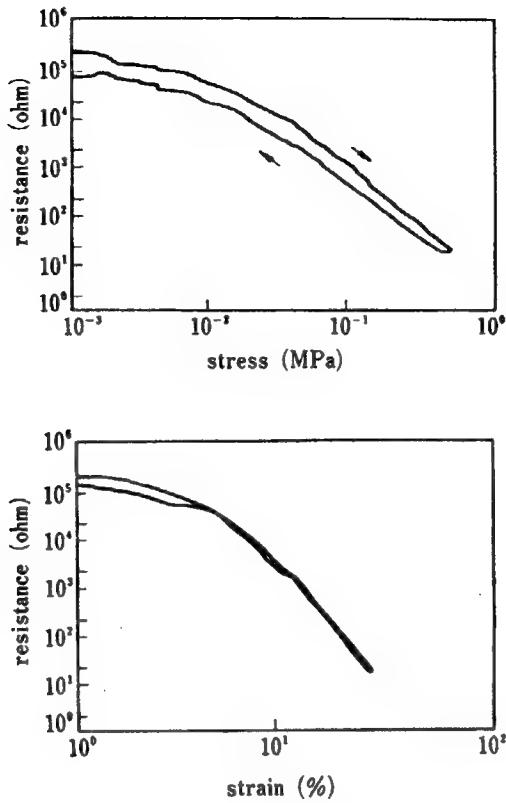


Figure 5. F-R and D-R Characteristics

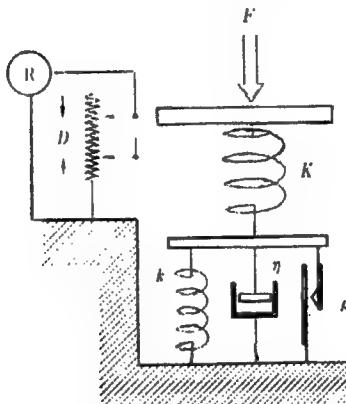


Figure 6. Viscoelasticity Model for Pressure Sensitive Conductive Rubber

In the TCS-5000, a leaf spring is placed on the substrate of the base to let it hold most of the external force. A warping in the leaf spring is converted to a change in the resistance by deforming a pressure sensitive conductive rubber inserted beneath the spring. This effect is obvious from a comparison between the F-R characteristic for a pressure sensitive conductive rubber alone (Figure 7) and the F-R characteristic for a leaf spring structure (Figure 8).

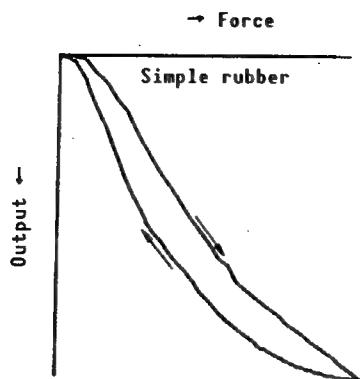


Figure 7. F-R Characteristic for Simple Rubber

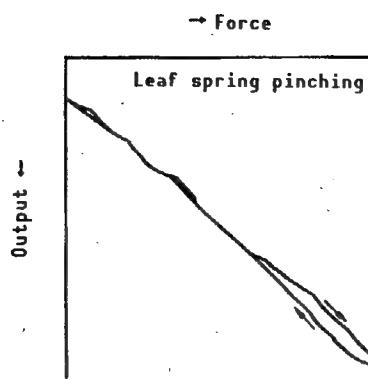


Figure 8. F-R Characteristic Within Leaf Spring

In the case of a TCS-5000 for practical use, a power source to be applied to a pressure sensitive conductive rubber, a circuit for converting a resistance change to an analog voltage output, a circuit for correcting the overall temperature change, etc., are assembled on a base substrate by the surface mounting technique (SMT) along with a sensing part.

(ii) Road sensor

The road sensor is for detecting the tread and the breadth, of the portion making contact with the earth, of a passing vehicle by means of the treading pressure of wheels of a vehicle. It is used to identify the types of vehicles on a toll road and at the gate of a pay parking lot. This product is not a device which utilizes the characteristic of an analog type pressure sensitive conductive rubber. Since it became feasible only after the CS series rubber achieved high durability and is interesting as a method of applying the pressure sensitive conductive rubber, it will be presented in the following. This element is basically a long resistor constant resistance per unit length on which a pressure sensitive conductive rubber is placed. Resistance is observed by burying the element across the road surface. When no treading pressure is applied, the resistance of the pressure sensitive conductive rubber is high so that the resistance of the resistor itself is observed. On the other hand, when there is treading pressure over a certain width of the device, the resistance of the pressure sensitive conductive rubber in that locality alone is reduced, short-circuiting that portion of the resistor. In other words, the reduction in the resistance of the device is proportional to the width of the treading part. As is clear from this function, the pressure sensitive conductive rubber of the road sensor acts as an on/off type device, and measurement with this device has an error factor naturally expected for an analog device. Nonetheless, with a trade-off between the resistance per unit length of a resistor and the lower limit of the width of the body to be measured, it is possible, even with an analog device, to control the error to a negligible amount.

The development of this sensor was prompted by the need to identify the type of vehicle by measuring the weight of a passing vehicle by means of an analog function. Since it was not possible to obtain weight measurement with satisfactory accuracy by the use of a pressure sensitive conductive rubber, a

system for discriminating the types of vehicles by measuring the width of the treading surface by the use of the above-mentioned element was proposed as an alternative.⁸

In an actual element, a flexible conductor that is divided into several parts is provided in order to measure the tread and the tread width of the wheel (Figure 9). Moreover, the sensor is designed so that the element is enclosed in a metallic groove in order to protect it from an extremely large treading pressure or a tire which is biting stones, and the treading pressure is applied indirectly by a spring member made of rubber whose compression is regulated.

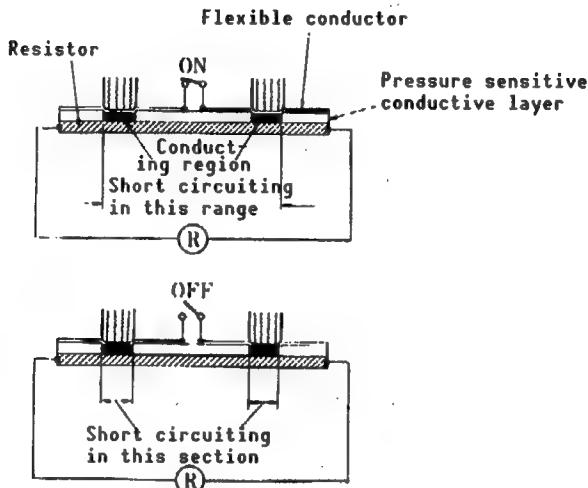


Figure 9. Principle of Operation of Tread Sensor

c. Tactile Sensor

In the field of robots, there is a strong demand for artificial tactility in helper robots and critical work robots (and manipulators) which are considered to be next-generation robots. Therefore, development of a distributed tactile sensor is very active, and the possibility of using analog type pressure sensitive conductive rubber in this field is being widely recognized.

A group of researchers of Tokai University developed a manipulator which can hold an egg between two plates which are opened and closed in parallel by the use of a sensor with a construction in which a CS sheet is inserted between two sheets of FPCs on which is printed a pattern of row and column electrodes in the form of a matrix.

In addition, the Product Science Research Institute developed a sensor which makes it possible to obtain the coordinates of the point of application of a pressurizing force on a plane and three-dimensional information on the strength of the pressurizing force (Figure 10).

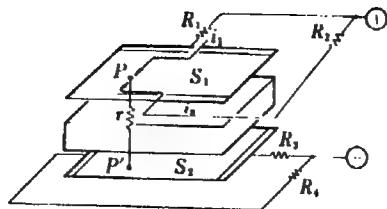


Figure 10. Construction and Principle of Operation of Tactile Sensor (Lower left)

When point P is pressed, current i_1 and i_2 flow in the circuit and their magnitudes can be measured as the voltage drops resistors R_1 and R_2 . From i_1 and i_2 the position of P in the plane S_1 can be determined. In addition, since the position of point P' in the plane S_2 can be known in the same way, the coordinates of point P in the plane can be determined.

Since the resistance and current for each of the paths $\Theta \rightarrow R_1 \rightarrow P$, $\Theta \rightarrow R_2 \rightarrow P$, $P' \rightarrow R_3 \rightarrow \Theta$ and $P' \rightarrow R_4 \rightarrow \Theta$ can be known, the voltage and the current (which is $i_1 + i_2$) between P and P' are known. Hence, the resistance r of the pressure sensitive conductive rubber which shows the strength of the applied pressure can be obtained.

In addition, our company has put on the market a pressure distributed image processing system which carries out real-time and various kinds of image processing, obtained by arranging serial connections (to prevent the creeping) of a CS and a diode in the form of a matrix, to obtain a video signal by sweeping the array. This system has actually been used in the field of human engineering and fields related to medical rehabilitation.

References

1. Voet, A., Sirkar, K. and Mullwns, T., RUBBER CHEM. TECH., Vol 42, 1969, p 874.
2. Kirkpatrick, S., REVIEWS OF MODERN PHYSICS, Vol 45, No 4, 1973, p 574.
3. Kanamori, K., INDUSTRIAL MATERIALS, Vol 30, No 6, 1982, p 67.
4. Ibid., U.S. Patent 4,273,682, 1981.
5. Technical Data of Yokohama Rubber Co., "Performance and Properties of Pressure Sensitive Conductive Silicone Rubber Sheet (CS57-7RSC)," 1980.
6. Shimojo, M. and Ishikawa, M., "Hysteresis Characteristic of Pressure Sensitive Conductive Rubber," collection of papers presented at Sixth Meeting of Japan Robotic Society, 1988, p 485.
7. Kanamori, K., Patent application published, 62-186019, 1987.

8. Ibid., 52-68437, 1977. .
9. Shimojo, M. and Ishikawa, M., "Detection of Contact Position and Load by Sheetlike Tactile Sensor and Their Applications," collection of papers presented at 11th Robot Sensor Symposium, 1988, p 65.

Ion Sensor

43067185g Tokyo SENSA GIJUTSU in Japanese Aug 89 pp 73-77

[Article by Shinichi Wakita, Government Industrial Research Institute, Osaka]

[Text] Ion sensors for measuring ion concentration in a solution are now being widely used in the fields of clinical, industrial and environmental measurement. The most popular type is the ion-selective sensor, and more than 20 kinds of electrodes are currently available commercially. The serum electrolyte measurement in the field of clinical tests has been carried out by flame photometry and coulometric titration. However, along with the standardization of serum for ionic electrode, blood electrolyte analyzers with built-in electrodes are spreading rapidly. Furthermore, an ion-selective field effect transistor (ISFET), obtained by combining ion-selective electrodes and a field effect transistor, which is an impedance converter, into one chip has been proposed. It is expected to be put to practical use as a sensor for monitoring, for instance, violently changing biomedical information *in vivo* and in real time. Since ISFETs can be manufactured according to semiconductor technology, it is easy to render them into superminiaturized and functionalized devices. Moreover, they have various features, e.g., they can be used for manufacturing intelligent sensors that are integrations of signal processing circuits.

The level of research on ISFETs in Japan is very high thanks to the pioneering work by Matsuo, et al. It was marketed for the first time in the world in 1983 by Kuraray Co., Ltd., in the form of pH and carbon dioxide sensors.

In this paper, the response mechanism of the ion sensors, R&D on ion sensor materials, ion sensor material fixing techniques, R&D of reference ISFETs and applications of ISFETs will be presented briefly as the latest trends in research on ion sensors. Further, as to the latest trends in research, the reader is referred to the more than 20 papers on ISFETs to be presented at the Fifth International Symposium (Transducers '89) to be held in Montreux, Switzerland this coming summer. A collection of papers from this symposium is scheduled to be published in SENSORS AND ACTUATORS at the end of this year. In addition, regarding optoload ion sensors using optical fibers, etc., and ion sensors using crystal oscillators that are actively being developed in recent years with optoelectronics in the background, the reader is referred to other survey articles.

1. Response Mechanism of Ion Sensors

An ISFET has a structure which cannot be explained in terms of the classical Nernst-Plank theory that takes the ion transport flux into account, and its sensor response mechanism is becoming a subject of academic interest. For a thin-film type ion sensor film which is characteristic of ISFET, the sensor property has been explained using the site-binding model that has the number of ion exchange sites in the insulation film and the acid dissociation constant and the basic dissociation constant of the insulation film as the parameters. However, for a thick-film type ion sensor film used for ion-selective electrodes, no clear-cut explanation has been proposed.

Sandifer¹ proposed a model which is an excitation of the site-binding model which takes the gel layer into consideration, discusses the response mechanism of an ion sensor including pH glass electrode. From the fact that a thin-film type ISFET can be made to show a satisfactory sensor response by transforming the surface through hydration, it will also be considered that a model that takes the gel layer into account is effective.

2. R&D of Ion Source Material

Development of excellent ion sensor materials occupies a very important position in the entirety of ion sensor research. For example, a pH glass electrode, as a result of vigorous search for the film composition materials with small error of alkali and excellent selectivity were developed, which led to the present popularization of ion sensors. R&D of the ion sensor materials has mainly been carried out in the field of ion-sensitive electrodes. Namely, the development of organic or inorganic ion conductive ion sensor materials, in particular ion sensor materials that are called organic neutral carriers, is very active. In contrast, development of insulating ion sensor materials that are characteristic to ISFETs is not as active.

As new inorganic ion sensor materials, the properties of ion sensors for heavy metals such as silver, copper, lead, cadmium, etc., that make use of chalcogenide glass, have been reported by Vlasov, et al.² This material is a conductive glass obtained by adding S_x and $AsSe_x$ to the conventional silver-based mixed conductor (MS/Ag_2S), and an improvement in stability and selectivity in the presence of strong acidity or redox material is obtained. Further, there is a report on the use of NASICON which is a super ion conductor of Na^+ to Na^+ ion sensor material.³

Olszyna, et al.,⁴ report a pH sensor obtained by depositing borazone (BN) by plasma CVD process to a thickness of about 1,000 Å on a film of silicon nitride which is the gate insulating film of an ISFET. The paper reports that the sensitivity is 50~59 mV for pH of 2~10, the response speed is 8 ms, the selection factor for Na^+ , K^+ , etc., is about 10^{-8} and that a device life of more than 6 months is obtained. Wakita, et al.,⁵ manufactured a pH-ISFET which uses a conductive titanium nitride (TiN) as the sensor material, by plasma CVD process, obtaining a sensitivity of 59 mV for pH 2~10.

As organic ion sensor materials, there are ion exchangers and neutral carriers which are electrically neutral. In particular, R&D in the neutral carriers is

active and many organic compounds with extremely high selectivity have been synthesized. At present, most of the Na^+ , K^+ , Ca^{2+} and Cl^- sensors for analysis of blood electrolyte sold commercially use organic materials.

Kimura, et al., report on 14 crown 4 derivative that shows an excellent Li^+ selectivity and the Li^+ determination in serum,⁶ and on that calyx [4] allene derivatives have an excellent Na^+ selectivity.⁷ Sugihara, et al.,⁸ report on the synthesis of phenanthroline derivatives and excellent Li^+ carriers. Kamata, et al.,⁹ report on the synthesis of thiuramdisulfide derivatives that have superior properties over the commercially available electrodes. Further, as one of very few research projects on neutral carriers for cations, there is the synthesis of a CO_3^{2-} carrier,¹⁰ and the future R&D in the field is anxiously awaited.

3. Fixing Techniques of Sensor Material to Device

Methods for fixing sensor materials to ISFET devices may be classified into dry methods such as evaporation, CVD and sputtering and wet methods such as casting and dip coating.

The dry methods are compatible with device manufacturing processes and have the feature that the film thickness can be controlled. Ito, et al.,¹¹ manufactured the well-known NAS glass by ion implantation process, and report the properties of Na^+ ISFET sensor in detail.

In contrast, the wet methods have considerable weaknesses when regarded as methods for manufacturing ion sensitive films. Nonetheless, one has to use the wet methods in order to fix numerous known neutral carriers that have excellent selectivity to the device. As a method for fixing these organic materials, it is common to manufacture an ion sensitive film by using polyvinylchloride (PVC), etc., as the film material. Although an organic ISFET can readily be manufactured by casting a PVC sensitive film on the gate part, there was a problem in that the service life of the sensor was short due to unsatisfactory adhesion of the PVC sensitive film to the device.

Bezegh, et al.,¹² focused their attention on solvents that are contained in the PVC sensitive films in large quantity, and propose ISFETs with long life by the use of solvents with high retention. Wakita, et al.,¹³ report that they obtained sensors with stabilized property for over 1 month by applying a lacquer sensitive film with excellent durability. Harrison, et al.,¹⁴ introduced about 6 percent of OH radical to PVC which is the material of the film, used SiCl_4 , formed a covalent bonding with the gate part according to the reaction scheme shown in Figure 1, and obtained an improvement in the service life. Recently, ISFETs in which polymers are covalently bonded by the use of silane coupling have been reported in succession.

Further, it has been pointed out that if a PVC film is coated directly on a silicon nitride film, localized pH changes are induced on the silicon nitride film due to permeation of carbon dioxide or ions of organic substances through the PVC film, causing errors in the sensor properties. Vlekker, et al.,¹⁵ manufactured an organic ISFET by coating a hydrogel containing a buffer

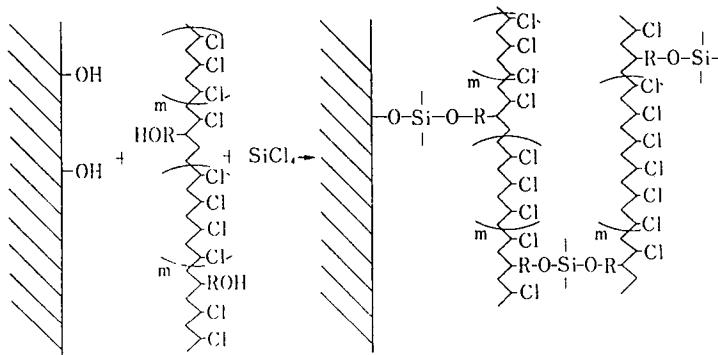


Figure 1. Reaction Scheme for Covalent Bonding Between Gate Insulating Film and PVC(OH)

solution on the gate insulating film and further dip-coating the PVC film, to alleviate the hindrance. Li, et al.,¹⁶ showed that the hindrance can be prevented by forming a silver and a silver chloride film on a silicon nitride film that responds to pH, and forming a PVC film on top of it. In addition, they confirmed that carbon dioxide and ions of organic substances permeate through a PVC film by an impedance method. To prevent such a hindrance, a variety of ideas are conceivable. However, a powerful solution to the problem is to form an electrode positively in the gate part of the ISFET, and as a result a structure similar to that of an ion-selective electrode will be obtained.

4. R&D on Reference ISFET

The biggest problem in the lag of putting ISFETs to practical use compared with ion-selective electrodes is the R&D on superminiaturized reference electrodes and reference ISFETs (REFETs). Kuraray Co., Ltd., and (Centron) Corp., currently selling ISFETs commercially, are using reference electrodes containing silane, etc., as an internal solution by manufacturing a small-sized silver/silver chloride electrode. However, the presence of an internal solution makes it inconvenient and reduces the advantage of a solid-state sensor to half. The current state of the reference ISFET may be summarized by saying that despite active R&D activities, only a few have so far been announced.

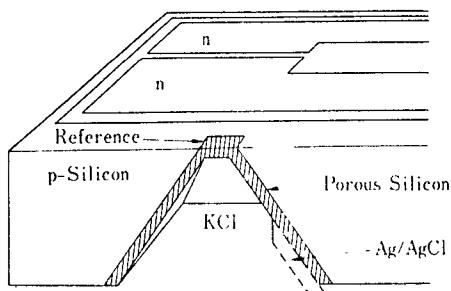


Figure 2. ISFET Integrating Ag/AgCl Electrode¹⁷

As one approaching method for manufacturing small-sized reference electrodes, a relatively large number of works on the manufacture of silver/silver chloride electrodes by micromachining, an IC technology, have been reported.

Smith, et al.,¹⁷ report a device which combines a silver/silver chloride electrode and an ISFET into one chip as shown in Figure 2. Since the silver/silver chloride electrode is a material for a sensor that responds to chloride ions as is well known, it is necessary to manufacture a liquid junction by providing an internal solution.

In order to manufacture a reference electrode that has no internal solution it is essentially important to develop new materials. A relatively large number of works on manufacturing REFETs by forming a hydrophilic polymer film on the gate insulating film of an ISFET have been reported. Van den Berg, et al.,¹⁸ examined the pH responsiveness by coating various kinds of polymers. As a result, they report that acrylic resins have satisfactory properties. One report says that ISFETs using silicone-based acrylic resins have a sensitivity smaller than 4 mV/pH for pH in the range of 4~8, and have a sensitivity of 12 mV/decade. Therefore, there seem to be some problems. Further, it has been reported that when a REFET was formed by developing an ITO film on the gate insulating film, and then causing an electrolytic polymerization in a solution into which styrene monomer is dissolved, the pH sensitivity on the acid side was almost nonexistent while the sensitivity on the alkali side was about 20 mV/pH.¹⁹ Yamaguchi, et al.,²⁰ manufactured a laminated film of Teflon and silver chloride by neutral sputtering to carry out basic examination of the reference electrodes that will not be affected by the ion intensity.

As another approaching method, Sugimoto, et al.,²¹ report on reference electrodes using ion pair compounds that have high solubility in oil. They are carrying out R&D on the PVC type reference electrodes that use similar ion pair compounds such as tetraphenyl boric acid and tetraphenyl arsonium salts. It is reported that these electrodes were not at all affected by Cl^- , ClO_4^- , Na^+ , etc., at pH in the range of 2~12, and a satisfactory result was obtained by combining them with pH-ISFET. Although there still remain some unsolved problems, these ion pair compounds for reference electrodes are hopeful materials partly because they are essentially not subject to the influence of ion intensity. Therefore, R&D on the REFETs which use such ion pair compounds will become active in the future.

5. Applications of ISFET

As application of ISFET to the clinical field, an ISFET with extraction of the electrode from the rear face was manufactured to measure pH within the oral cavity by burying the ISFET in an artificial tooth.²² There is a report on three examples of ex vivo monitoring of Na^+ , K^+ , Ca^{2+} and Cl^- of a patient during cardiac surgery by a continuous surgery of the patient's blood with a circulation circuit outside the body.²³

Tamura, et al.,²⁴ developed a circulation device outside the body which can measure pH of the blood over a long time without making direct contact with the blood and without being subjected to the effect of the ISFET drift by the use of hollow fibers upon noticing that the response time of the ISFET is very small.

It should be mentioned that as applications of ISFET there have been reported many studies on enzyme FETs obtained by fixing enzyme films on the gate. However, the reader is referred to other survey articles on this subject.

In the foregoing, the latest trends in research on ion sensors have been sketched centering around the reports that have been published during the past 3 years. Undoubtedly, there are still many useful research projects not included in the present survey for which the writer begs forgiveness of each author.

R&D of ion sensor materials has reached a stage at which molecular design is feasible. The imminent targets of the technical development of ISFETs will be to establish techniques for fixing the neutral carriers to ISFET devices and R&D of the reference ISFETs.

References

1. Sandifer, J.R., ANAL. CHEM., Vol 60, 1988, p 1533.
2. Vlasov, Yu.G. and Bvchkov, E.A., SENS. ACTUATORS, Vol 12, 1987, p 275.
3. Fabry, P. Gros, J.P., Brodaz, J.F. and Kleitz, M., Ibid., Vol 15, 1988, p 33.
4. Olszyna, A., Wosinski, W., Sobczynska, D. and Torbicz, W., J. CRYSTAL GROWTH, Vol 82, 1987, p 757.
5. Wakita, Makabe, Mochizuki and Azuma, 58th Spring Meeting of the Chemical Society of Japan, Collection of Preprinted Papers I, 1989, p 360.
6. Kimura, K., Oishi, H., Miura T. and Shono, T., ANAL. CHEM., Vol 59, 1987, p 2331.
7. Kimura, K., Matsuo, M. and Shono, T., CHEM. LETT., 1988, p 615.
8. Sugihara, H., Okada, T. and Hiratani, K., Ibid., 1987, p 2391.
9. Kamata, S., Bhale, A., Fukunaga, Y. and Murata, H., ANAL. CHEM., Vol 60, 1988, p 2464.
10. Meyerhoff, M.E., Pretsch, E., Welti, D.H. and Simon, W., ANAL. CHEM., Vol 59, 1987, p 144.
11. Ito, T., Inagaki, H. and Igarashi, I., IEEE Trans. on ED-35, 1988, p 56.
12. Bezegh, K., Bezegh, A., Janata, J., Oesch, U., Xu, A. and Simon, W., ANAL. CHEM., Vol 59, 1987, p 2846.
13. Wakida, S., Yamane, M. and Hiro, K., SENS. MATERIALS, Vol 2, 1988, p 107.

14. Harrison, D.J., Cunningham, L.L., Li, X., Teclemariam, A. and Permann, D., J. ELECTROCHEM. SOC., Vol 135, 1988, p 243.
15. Van den Vlekkert, H., Francis, C., Girsel, A. and de Rooij, N.F., ANALYST (London), Vol 113, 1988, p 102.
16. Li, X., Verpoorte, E.M.J. and Harrison, D.J., ANAL. CHEM., Vol 60, 1988, p 493.
17. Smith, R.L. and Scott, D.C., IEEE Trans. on BME-33, 1986, p 83.
18. Van den Berg, A., van der Wal, P.D., Ptasinski, M., Sudhölter, E.J.R., Reinhoudt, D.N. and Bergveld, P., Proceedings of Second Int. Meeting on Chemical Sensors, 1986, p 419.
19. Takahashi, Osada, Shinohara and Ono, 55th Fall Meeting of Chemical Society of Japan, Collection of Preprinted Papers II, 1987, p 64.
20. Yamaguchi, Lichida, Shimomura, Ishizuka and Katsume, Eighth Chemical Sensor Research Meeting, Collected Abstract of Papers, 1989, p 9.
21. Sugimoto, Tokura, Toda, Suzuki and Shirai, 56th Spring Meeting of Chemical Society of Japan, Collection of Preprinted Papers I, 1988, p 608.
22. Van den Vlekkert, H.H., Koeck, B., Prongue, D., Berthoud, J., Hu, B., de Rooij, N.F., Gilli, E. and de Crousaz, Ph., SENS. ACTUATORS, Vol 14, 1988, p 165.
23. ELECTRONICS INDUSTRY MONTHLY, Vol 27, 1985, p 38.
24. Tamura, T., Togawa, T., Suematsu, K. and Sato, K., SENS. ACTUATORS, Vol 16, 1989, p 273.

Problems in Large-Diameter Wafer Production

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[Article by Shin'ichiro Takasu]

[Text] 1. Introduction--Current Status, Demands

Among the problems which arose with the early use of 200mm wafers in 1984 and 1985 was so-called silicon recession, a problem which, on the surface, subsided in 1986. The announcements concerning 1M DRAM development and production and 4M DRAM development which came in 1986 and 1987, however, pointed strongly toward increasing chip sizes.¹ The author, assisted by Mizoue of Oki Electric and Hashimoto of Hitachi in SEMI's long-term planning committee, predicted the move to the 200mm diameter in 1992 from related analyses.²

Since proposing a 200mm wafer standard to SEMI in 1982, IBM had remained silent, but in 1988 it announced the introduction of 200mm wafer processes at a SEMI technical seminar.³ Monsanto (now MEMC) went public with Sematech's current practices and future specifications relative to the 200mm wafer.⁴ These announcements spurred a trend toward adoption of 200mm wafer processes.

In May, 1989, Ozawa prepared an outlook to the year 2000 for the DRAM in the ECS, foreseeing a chip area of 461 mm² and a capacity of 1G bits by 2000.⁵ Siu, at the same time, argued that microprocessor chip sizes would become unavoidably larger due to the large cache memories that will be incorporated, but did not predict any specific size.⁶ At the SEMI technical seminar held in Osaka in June, the pros and cons of larger wafer size were debated from the perspectives of economy, processes, and process combinations.⁷

This trend is clearly revealed in the results of a questionnaire survey which the Japan Electronic Industry Development Association conducted among related academic and industrial associations from December, 1988, to January, 1989.⁸ According to this survey, the initial use of 200mm wafers is concentrated in 16M DRAM production. With respect to this 16M DRAM

production using 200mm wafers, it is predicted that companies will start making [fabrication] equipment in 1989-1990, the wafers in 1990-1991, and the devices in 1991-1992, with respective 1-year time delays. These wafers are grown by the CZ method, and it is predicted that epi[taxial] wafers will most likely be used. MCZ utilization is also foreseen, but not FZ. Despite the larger wafer size, the characteristics needed to cope with 16M DRAM production are being demanded. More specifically, site flatness, of course, and the ability to cope with a design rule of $0.6 - 0.5\mu$ are demanded. Many questionnaire respondents pointed to various problems, such as uniformity in wafers and production processes, process-induced problems such as heavy-metal contamination and crystal defects during dry etching, and problems created by process automation. How to resolve these problems was the main subject considered at the SEMI technical seminar mentioned above. To the question of whether or not moving to the 200mm wafer would really be economical, both Komiya⁹ and Nagano¹⁰ clearly articulated the superiority of the larger wafer. The most frequent answer concerning the probable wafer size in the year 2000 was 250 mm, but quite a number predicted a size of 300 mm.

In the area of problems arising from design considerations, there is a demand for faster microprocessors with larger registers, and, along with such microprocessors, faster DRAM's. As a result, the spotlight moves to bi-CMOS or CMOS chips using N-type wafers.^{5,6} This trend will probably have a pronounced influence on silicon crystal growth. These trends are summarized in Table 1, prepared from the papers of Ozawa, Siu, Komiya, Nagano, and Nakamura mentioned above. In considering these trends, we will narrow our focus to those problems involving silicon wafers.

Table 1 Technical Trends in ULSI's

DRAM Memory Capacity	200 kbit	1 MBIT	4 MBIT	10 MBIT	14 MBIT	256 MBIT	1 GBIT
Design Rule (μm)	2-1.5	1.25-1.0	0.8	0.5	0.4	0.3	0.2
Chip Area (mm^2)	40	80	91.1	137	205	307	461
Diagonal Length(mm)	10	12.26	15.8	18.5	22.0	27.7	33.8
Exposure Light	g, i	g, i	i	i	i	Eximer	Eximer, X
Form	Stepper	Stepper	Stepper	Stepper	Stepper	Stepper	Stepper
Orientation	DF	DF/notch	DF/notch	DF/notch	DF/notch	DF/notch	DF/notch
Diffusion Furnace	N	N / V	V / N	V	V	V	V
Collating	IC, IC	IC, IC	IC	IC	IC	IC	IC
Paticulate Limit(nm)	200	150	80	50	40	30	20
Wafer Dia. (cm)	12.5	15/12.6	16	20	20/25	25	25/30
Thickness (μm)	550	825/550	825	725	725/775	775	775/825
Weight (gr)	15.8	25.8/15.8	25.8	53.3	53.3/89	89	89/132
Croving Method	CZ/EPI	CZ/EPI	CZ/EPI	CZ/EPI	CZ/EPI	CZ/EPI	CZ/EPI
Production Start	1984	1987	1989	1992	1995	1998	2001

2. Crystal Growth Problems

As diagrammed in Figure 1, we assume that a weight W_c crucible is charged with polycrystalline and pulled up 100-percent. When growing crystals, from transmitting and eliminating transitions, etc, cones are formed at the seed and tail parts having heights of H_1 and H_2 (in units of radii), respectively. Due to the development of minute defects, and to instability in oxygen concentration, immediately below the seed cone, a portion develops which cannot be used, i.e. roughly $H_2 \times \text{radius}$. Also, crystals are grown with about 5-percent extra diameter to allow for diameter control. Accordingly, this weight is always minimally added to the weight of the crystal portion which can be used. In some cases, due to increased impurities concentration, etc, portions develop also in the tail which cannot be used in full diameter. With an extra diameter ratio of 1.05, $H_1 = 0.25$, $H_2 = 0.5$, and $H_3 = 2$, the weight, in kg units, of the portions of the cone and immediately below the cone which cannot be used comes to 23.4 kg. In actual practice, about 85 percent of the charge can be pulled up. Calculating with this point in mind, we get 27.5 kg. The yield in this case will not exceed 73.4 percent, even though we increase the charge without limit. When K_{eff} is small, it is necessary to consider the resistance distribution in the growth direction. The results of calculations done in this case are plotted in Figure 2.

Figure 1 Effective Parts in Growing Si Crystals

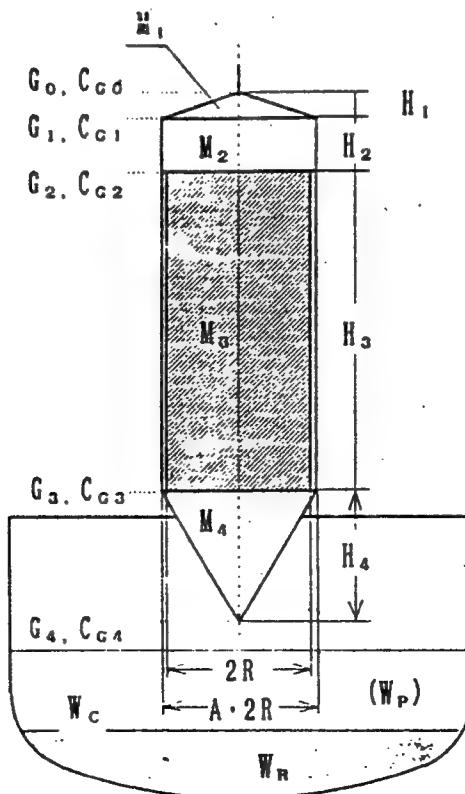
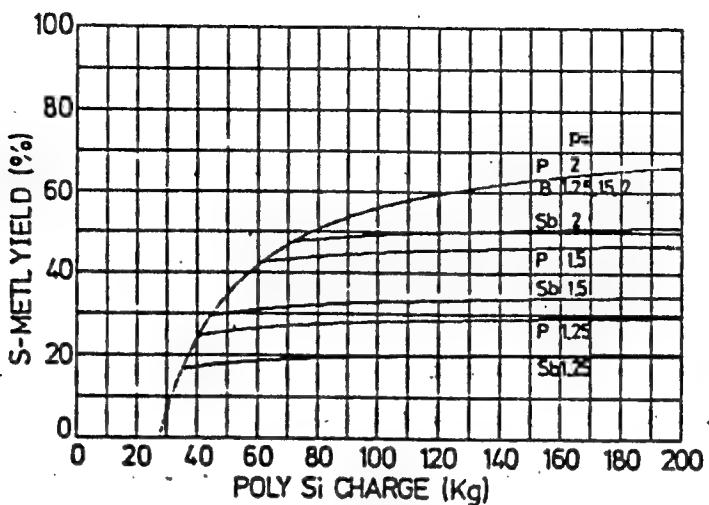


Figure 2 Relation Between Effective Single Crystal Yield vs Polysilicon Charge



As may be understood from the figures, a charge of about 100 kg or more is desirable for p-type wafers, but we notice that things are a little different for the n-type. Yield increase when the specific resistivity of P and Sb are low compared to B is almost non-existent at and beyond the point at which there is a change to the silicon charge limit. In other words, almost no high-volume charge effect is exhibited, and we see that the n-type silicon cost rises. One thing that both [types] have in common is that the silicon expands when it solidifies, so that the crucibles ordinarily cannot be used many times. This is another factor that contributes to rising costs and is particularly influential with the n type. In this calculation it is assumed that there is no change in the use constant during crystal pulling, that there is no interaction with anything outside the system, and that natural solidification takes place. Accordingly, if these assumptions can be changed, then some clues to [a solution to] this problem might be found. We will next consider several different methods.

(1) Charging Method

As shown in Figure 2, the yield will not rise after reaching the resistivity limit, so a tail cone is made a little past the point of transition and taken out of the furnace. Then polycrystalline silicon is added to the initial charge quantity, inclusive of dopant(s), and crystal pulling is done repeatedly. The effectiveness of this method is great in view of its simplicity of equipment and technology. There is, however, no way to avoid the seed and tail cone losses. A high-purity grade of granular polycrystalline silicon that is made with a fluidized bed technique and suitable for recharging has recently been developed and put on the market. This method was previously held suspect due to worries over increasing heavy metal

contamination in conjunction with increases in n , but in tests there was no change in purity through the first four uses.

(2) Continuous Charging

In the formula $C_g = K_{eff}L_0(1 - g)^{K_{eff}-1}$ that represents the change in the concentration of impurities added during pull up, if we make $L_0(1 - g)$ constant irrespective of g , C_g becomes constant. For this purpose, one need only continuously add polysilicon, inclusive of dopant, according to the pulling weight. Polycrystalline granules, and polycrystalline rods, in solid and molten form, may be considered for the additive form. The granular silicon mentioned in the previous section is extremely disadvantageous for this addition, and has been the subject of recent developmental research. The liquid concentration rises, so non-additive silicon may be added, but it is necessary to adjust the addition amount according to the respective K_{eff} values.

(3) Double Crucible Method

This is a method in which, in principle, a double (inner/outer) crucible is connected to a slender pipe for controlling diffusion, and crystal pulling is performed in the inner crucible. This method has been applied by Lin to silicon.⁹ One problem with this method is the cost of making the double crucibles. Kida *et al.*, however, have sought to remedy this problem by using an inner crucible that can be raised and lowered.¹⁰

(4) Vaporization Control Method

When there is dopant vaporization, the rise of dopant together with pull up can be checked, and the concentration held constant. Brice has devised the following formula for vaporization.

$$C_g = K_{eff}[B - \{B - CLO\}(1 - g) + (x/fv)]$$
$$B = \epsilon ACE/x \quad x = fv(K_{eff} - 1) + \epsilon A$$

where ϵ is the evaporation factor, A is the free surface of molten material inside the crucible, fv is the volumetric growth velocity, and CE is the mean concentration.¹¹ Accordingly, it is theoretically possible to achieve growth at constant concentration throughout the entire pulling length. In tests this has been applied to antimony.

(6) [sic] Combinations, Other

There is ample significance in combining the aforementioned methods. As has already been pointed out, one example of this is the combination of continuous charging and vertical magnetic fields. There is hope with this method of effectiveness that is not merely additive. It has been reported

that K_{eff} increases when crystals are pulled under the influence of a magnetic field.¹²

One big problem accompanying larger scale is the great effect which the thermal environment has on crystal quality. As Rea *et al.* have pointed out, high-speed pulling is one method of obtaining high-quality crystals.¹³ The pulling speed is proportional to the difference in the products of the temperature gradient in the vicinity of the interface and the respective coefficients of thermal conductivity at the interface between the molten material and the crystal. Hence the speed of crystallization can be speeded up either by reducing the temperature gradient in the molten material or increasing the temperature gradient in the crystal. Rea *et al.* stipulate a passage speed in the 900-700°C range, besides the pulling speed, so it is necessary to exercise adequate care with respect to the interference of the pulling speed and thermal history.

3. Problems in Crystal Processing, Shipment

As is shown in Table 1, we can have both larger diameters and higher flatness. This flatness, moreover, involves many problems, from those concerning terminology and definitions¹⁴ to those concerning measurement. The number of measurement points is particularly problematic for large exposure areas. This is now being studied by SEMI. Since the way of taking this flatness and the focusing method are different in different exposure units, it becomes necessary to make measurements with methods that match each case. The so-called flatness decision tree has been proposed as a way of resolving these problems, and has actually been adopted.¹⁵ Another problem with larger wafers is the difficulty of measuring "warp" at 150 mm and above.¹⁶ With the JIS-specified method(s), accurate measurements cannot be made due to the effect of weight. SEMI has been doing a series of tests on measurements made while maintaining [wafers] in a free and roughly vertical condition.

The dominant method used currently is a batch method employing polishing with free sand granules. The wafer-by-wafer method is also gradually being implemented. With the wafer-by-wafer method, the polishing wheel diameter can be small, and it is thought to be easier to maintain satisfactory precision. This method is also superior in performing mixed processing on wafers of various diameters, and in controlling each individual wafer. Flatness shipment control can be implemented with maximum value control, distribution designation control, or median value control, but it is the functions of the measurement control equipment that are important.

Eichinger *et al.* have recently employed total-reflecting x-ray fluorometric analysis equipment in analyzing the heavy metals on wafers. They report success in obtaining a sensitivity of 10^{12-11} atoms/cm².¹⁷ They further report that, by incorporating the method of Shiraiwa *et al.*,¹⁸ they can reach the level of 10^{8-9} atoms/cm².¹⁹ It is hoped that further progress will

be made with this method. Hockett, meanwhile, has demonstrated with this method that heavy metal contamination arises from shipping carriers.²⁰ The cause is thought to originate with the methods and catalysts used in manufacturing the synthetic resins used in the shipping carriers.

4. Problems Which Arise in Crystal Use, Wafer Fabrication

4-1 Peripheral Round & BSD Processing

As wafer size increases, the weight increases, so impacts occur with the conveyor equipment, carriers, or boats in the transport system, which results in wafer chipping. Minute silicon granules have been found among the minute particle contaminants in the wafer periphery, and these are thought to cause chipping. The results of such observations suggest that polishing the edges to a mirror finish would be effective. It is also very likely that BSD is a source of minute particle generation, and attention is now being given to the method of polysilicon adherence with a CVD technique on the back side as a method of gettering to replace BSD. With this method, when the adhering technique is poor, it is possible that it will also become a source of minute particle contamination. It can also cause wafer warping, so care should be exercised.²¹

4-2 Heat Treatment, Oxygen, Crystal Growth Conditions

Crystals grown with the CZ or MCZ method contain oxygen in an amount ranging from 2×10^{17} to 2×10^{18} atoms/cc (old ASTM equivalent coefficient). Accordingly, oxygen donors are generated by heating to 450 - 475°C. When large-diameter wafers are heat-treated in a horizontal diffusion furnace, stagnation near the furnace door and vertical temperature differences near the furnace door result in differences in oxygen donor generation, which can affect the resistance distribution. This needs to be watched for, particularly with high-resistance p-type wafers. This kind of problem did not arise in the vertical diffusion furnace.

When the oxygen content exceeds 1.4×10^{18} atoms/cc, the precipitation of silicon oxide may be observed, depending on the heat-treatment conditions. Such precipitation can also be caused by heat treatment at lower concentrations. Intrinsic gettering (IG), in which this precipitation is employed, is being used with considerable effectiveness. It is well known that, in these cases, there are variations in the quantity and speed of precipitation even with the same oxygen concentration. The cause was conventionally thought to lie in the thermal history, but more recent research has shown that the surface vicinity is also affected by surface heavy metal contamination.

It has been thought for some time that the oxygen concentration and thermal history contribute to oxygen precipitation and bulk SF (BSF). As noted above, however, heavy metals are also involved. Furthermore, as pointed out

by Rea, it has also become clear that the pulling speed is also involved. Suzuki noticed that BSF was generally low with the MCZ method, and that there are cases when BSF develops during high-speed pulling. He therefore conducted experiments in which he demonstrated that this is very much involved in pulling speed and fluctuations therewith.²² This phenomenon can be explained in terms of remelting.

5. Concluding Remarks

We have discussed above the causes of making silicon wafers larger and the problems associated therewith. The 200mm process has just now gotten on track. Unforeseen problems may still arise. Factors of throughput and yield can make it difficult to resolve even those problems which can be predicted. Judging from recent trends, it is possible that a fair number of these problems can be resolved through computer simulation. With many of these problems, such as precipitation and BSF generation, it is necessary to take a fairly theoretical approach toward resolving them. This suggests the need for continued cooperation between industry and the academic societies.

References

1. For example, "4M DRAM no Zenbo," in *Nikkei Microdevices*, Special Issue, 87-1, 1987.
2. S. Takasu, *SEMI Choki Keikaku Iinkai Shiryo*.
3. D. I. Golland, *SEMI Step Meeting Technical Proceedings*, p 102, SEMI, 1988.
4. G. E. Thyng, *SEMI Step Meeting Technical Proceedings*, p 154, SEMI, 1988.
5. O. Ozawa, *ECS Extended Abstract*, 89-1, p 181, ECS, 1989.
6. W. M. Siu, *WCS Extended Abstract*, 89-1, p 179, ECS, 1989.
7. M. Nakamura, Y. Nagano, et al., *Technical Proceedings Semicon/Osaka 1989*, p 241-323, 1989.
8. Japan Electronic Industry Development Association: *Ueha Daikokai Gijutsu Doko ni kansuru Chosa Kenkyu Hokokusho I*, 1989.
9. K. E. Benson, W. Lin & E. P. Martin, *Semiconductor Silicon*, 1981 ed. by H. R. Huff, R. J. Kriegler & Y. Taleishi, p 33, ECS, 1981.
10. M. Kida, Y. Arai, N. Ono & K. Sahira, *ICCG-9 Abstract*, No 23aC06, p 230, 1989.

11. J. C. Brice, *The Growth of Crystals from Liquids*, p 248, North-Holland, 1973.
12. K. Hoshi, S. Izawa, et al.: *Dai-20-kai Handotai Senmon Koshukai Yokoshu*, p 183, 1983.
13. S. N. Rea & H. M. Grimes, *ECS Extended Abstract*, Vol 87-1, p 98, 1987.
14. Japan Electronic Industry Development Association: *62-M-258 Shirikon Ueha Heitando ni kansuru Yogo*.
15. *1989 SEMI International Standards, Materials*, SEMI, 1989.
16. K. Aoshima, J. Yamazaki, et al.: *Gakushin 145 I, Dai-46-kai Kenkyukai Shiryo*, p 32, 1989.
17. P. Eichinger, R. J. Ruth & H. Schwenke, *Semiconductor Fabrication*, ed. by D. C. Gupta, p 305, ASTM, 1989.
18. T. Shiraiwa, H. Fujino, S. Sumita & Y. Tanizoe, *ibid*, p 314.
19. A. Huber, H. J. Ruth, P. Eichinger, Th. Bauer, L. Kotz & R. Staudigl, *Diagnostic Techniques for Semiconductor Materials and Devices*, ed. by T. J. Shaffner & D. K. Shroder, p 109, 1988.
20. R. S. Hockett, personal communication.
21. G. Borionetti, M. Domenici & G. Ferrero, *Semiconductor Fabrication*, ed. by D. C. Gupta, p 400, ASTM, 1989.
22. O. Suzuki & S. Takasu, to be published.

Outlook for Package Technology

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[Article by Yasuyoshi Kuniyatsu]

[Text] The IC packages which serve as containers for semiconductor integrated circuits (IC's) generally come in three typical structure types, according to the sealing material used, namely the meta-sealed ceramic package (laminated ceramic package), the glass-sealed ceramic package (pressed ceramic package), and the plastic-molded package.

We will describe the manufacturing process for the ceramic packages only (cf Figure 1). We begin by describing the manufacturing process for the laminated ceramic package.

First, as additives to the alumina, flux is pulverized and mixed, after which a bonding agent (binder), plasticizer, and solvent are mixed in, forming a slurry, from which a tape-form material is molded using a molding technique called doctor blade.

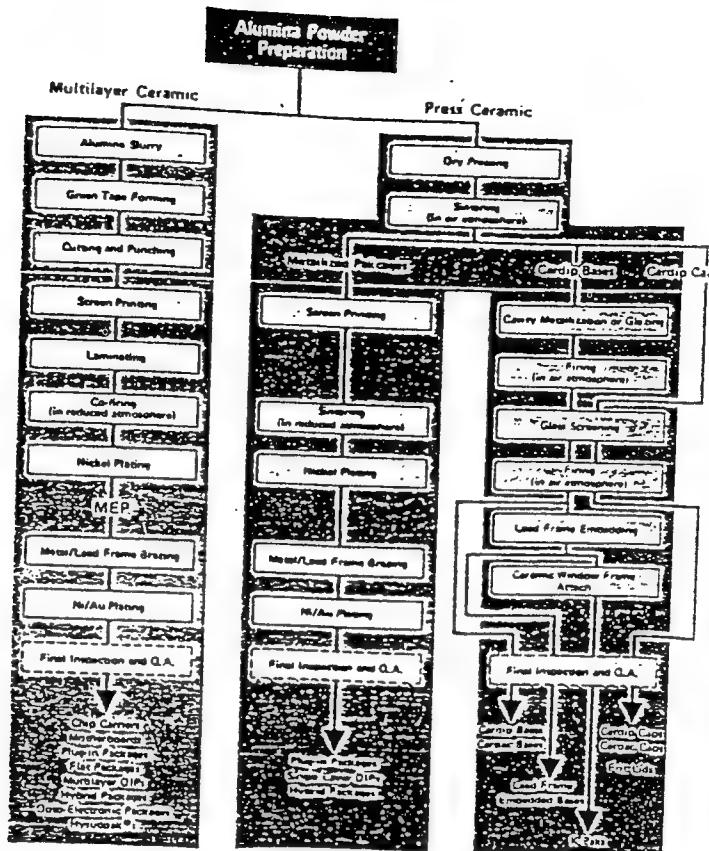
This is followed by the so-called green processes of cutting and punching the material into the desired size. It is during this process that the positioning holes which will be used in subsequent lithographic and lamination processes are made, as well as the through-holes (viaducts) to provide for vertical conduction, are made.

Then, by means of screen printing, with Al_2O_3 and a conducting paste of a high-melting-point metal such as tungsten or molybdenum, and using the alumina paste which is used as a raw material in the insulative layers, printing is performed to the proper controlled thickness.

After the layers have been printed, they are laminated into a single unit under the requisite temperature and pressure.

Then the moldings, either in single form or unified in a connected array, are baked at high temperature in a moisture-added reducing atmosphere. It

Figure 1 Process Flow



is in this stage that (1) the resin components needed during green processing are thermally decomposed and (2) the conducting layer(s) is/are metalized and the ceramic material is baked. This is called cofiring.

After this, depending on the package type, the hardware and terminal metal are soldered on. Finally, depending on the chip type, a nickelplating or goldplating process is performed to render the device able to withstand high temperature and high humidity during use, and able to satisfy the common packaging processes (chip mounting, bonding, sealing, etc). The package is then complete.

The pressed ceramic package, meanwhile, is made of raw materials prepared mainly of alumina or silica powders, to which a binder has been added. This is pulverized and suspended in a liquid, then spray-dried with hot air.

The granular material pulverized in the drying process in this manner is then molded under pressure, using a metal mold. The binder is then removed in an oxidizing atmosphere and the material is baked.

For the pressed ceramic package, a paste of silver, gold, or glass is baked onto the central part of the base ceramic where the chip will be mounted. Also, gas is printed [sic] on the sealed part on the ceramic [base], and this is similarly baked.

With respect to finishing, the lead frame is assembled by glass welding, and, depending on the demand, the lead frame is processed and finished into "J" or "gullwing" shapes.

Compared to ceramic packages, plastic packages are said to be deficiently reliable in the following particulars.

- (1) The plastic directly covers the chip area.
- (2) Plastics are characteristically permeable to water.
- (3) Plastics have coefficients of thermal expansion that differ greatly from those of the semiconductor chip and packaging material.

Encumbered by these properties, plastic packages tend to absorb moisture (depending on the time elapsing before mounting and the storage environment). When they are subsequently heated in the mounting process, peeling occurs, resulting in cracks and poor reliability.

Ceramic packages, on the other hand, are basically sealed airtight and hence do not suffer these shortcomings. They are accordingly the package of preference for high-reliability, high-performance devices and newly developed IC products.

Since laminated packages are made in tape form, they can be made into all kinds of shapes, and are thus very flexible to different user needs and offer unlimited growth potential. A surface-mounting type package has been developed also, which uses a pressed ceramic called *CER DIP* [from phonetics] and is sealed with low-melting-point glass. This package has now reached the production state and is coming into increasing demand.

2. Ceramic Package Classification

Ceramic packages may be classified according to shape and mounting technique (cf Figures 2 and 3). Figures 2 and 3 not reproduced.

We will discuss the shape-based classification of laminated ceramic packages in greater detail, looking first at the multi-layer ceramic type.

[I. Multi-Layer Ceramic Type]

A. Side-Brazed Package

This is the laminated package commonly called DIP (dual in-line package). The standard device has a 100-mil pitch. There are also 50-mil and 70-mil Schering [from phonetics] types.

There is a special type of package called the bottom-brazed type. (There are also types in which the soldering positions come to the back of the substrate.) Almost all of the standard types have been implemented in plastic, but [ceramic] is still used in chips where high quality is demanded. These are unsuitable for surface-mounted packages, however, because through-holes in the substrate are used to make contact with the substrate (inserting them into sockets or mounting them directly onto printed circuit boards). The package area is large compared to the number of leads, making it poorly suited to high-density mounting environments.

B. SO Package

This package has the same shape as the DIP type, with gull-wing type leads. It is called a small outline integrated circuit (SOIC or simply SO) package. This package began to appear in electronic timepiece applications around 1970. It is easy to use, just as the DIP, and is mostly implemented in

plastic, although there is also a demand for the ceramic type. This package can be mounted on a printed circuit board, and is a promising type as a surface-mounted package.

C. LCCC (Leadless Ceramic Chip Carrier)

As is well known, this package was the first surface-mounted package, appearing in the 1970's. It has but 1/6th the area and 1/10th the weight of an ordinary DIP, and is a high-quality laminated package for high-integration implementations.

According to JC-11 (Junction-11) of the JEDEC (Join[t] Electron Device Engineering Council), dimensional standards are made in four LCC[C] classifications. The devices are used for many different purposes and applications, primarily in the United States.

The standard lead intervals are 40 and 50 mils, although 25-mil devices are also produced. The biggest problem in using these packages is the mismatch resulting from the difference in thermal expansion with the printed circuit boards. Intense work is being done to develop print boards in which this problem is resolved.

D. Flat Package (Including Bend Type)

This is a laminated package in which leads are extended from all four sides. The standard lead pitch is 50 mils, but 20-mil and 25-mil pitches are also used. The package comes in a top-brazed and a bottom-brazed type, according to the soldering points. The leads can be placed directly on the pad of a printed circuit board, making it ideal for surface-mounted packages. It is also easy to use because the mounting procedures (chip mounting, wire bonding, etc) are very similar to those used for DIP types. The trend toward more pins is being promoted, but that makes it difficult to do the necessary electrical checks and other tests, and also makes chip-handling and transport more problematic. For this reason plastic is being used to make simpler carriers. Bend type packages are also being made and are expected to find a growing market.

E. J-Bend Type CC

This is a laminated package in which the surface-mounting concept has been implemented more thoroughly. With flat packages, lead frames that extend so as to become long are unnecessary in terms of raising density, and have come along in response to the demand for mounting devices in which greater reliability is required. There is both a J-type and an E-type.

Among PLCC's, this package is standardized by JEDEC. Both 40- and 50-mil pitch types are produced, constituting a group of packages that is growing

very rapidly in the United States. This package has a high performance/cost factor, and is expected to find a growing market.

F. Pin Grid Array Package

This is a package which has pins extending from the entire back surface and features a greater number of I/O pins. The package is made with 50-mil and 100-mil pitch, and in two structural types, namely cavity-down and cavity-up (with the chip-mounting side being on the same or opposite side, respectively, as the pins). The number of I/O's can be increased, and great freedom of terminal arrangement is afforded, making it unrivaled among laminated packages in terms of shape and wiring freedom. Plastic packages have recently appeared also, with some producers orienting their products toward the consumer goods markets.

This type of package must be mounted on a printed circuit board using a socket or through-holes, and is not believed to be suitable for surface mounting.

G. Small-Pin Pin Grid Array

A pin grid array package has recently been made in which the pin length is shortened and the package rendered suitable for surface mounting while maintaining the advantages of the pin grid array package discussed above in section F. It is thought that this now represents one new direction in which package structure will develop.

H. Pad Array LCC

Another package which is thought to be a trend-setter is the pad array LCC. This is a surface-mounting type of laminated package in which the I/O terminals are taken out the back, as in the pin grid array, but no pins are used on the back, with contacts being made by metalization only.

We next look at the pressed ceramic packages and their classification by package shape.

[II. Pressed Ceramic Packages]

A. CER PAC, SO Package

This is a package which uses pressed ceramics and has leads coming out from two directions. It is thus a dual in-line type, like the laminated [DIP] type. The CER PAC has been known for quite some time as a small, thin, and highly airtight package. This is also true of the SO package. In particular, this package is made in shapes that follow those of the EIAJ (Electronic Industries Association of Japan) and JEDEC plastic packages. SO type packages with "J" leads have also appeared in recent years.

B. Quard CER PAC, CER-QUAD

These are pressed ceramic packages which have leads extending from all four sides. The number of pins is increased by having leads exist on all four sides and using a fine pitch. In terms of lead shape, two varieties are commonly known.

(1) "J" Lead: In this configuration, the leads are formed in the shape of the letter J on the bottom side. This type is PLCC-compatible. The most common models have 28 - 84 pins at 50-mil pitch.

(2) Gullwing: In this configuration, the leads are formed in the shape of the letter L on the outer edges of the package. It can be implemented with a large number of pins, using small pins and fine pitch. In terms of pin pitch, the choices are 1.0 mm, 0.8 mm, and 0.65 mm, proposed as non-QFP types by the EIAJ, and the 50-mil and 25-mil pitches used mainly in the United States.

In terms of structure, there are the 2-layer (CER DIP) and 3-layer (K-PACK) types, diagrammed in Figure 4. The 2-layer type is sealed with a non-crystalline, low-melting-point glass (sealing temperature = 420 - 460°C) that is printed on pre-molded ceramic pieces called the base and the cap, respectively.

The 3-layer type is structured with ceramic pieces called the base, [the cap,] and the window frame, respectively, assembled with a crystalline glass together with the leads. The cap is resealed with glass, epoxy resin, or Au-Sn solder.

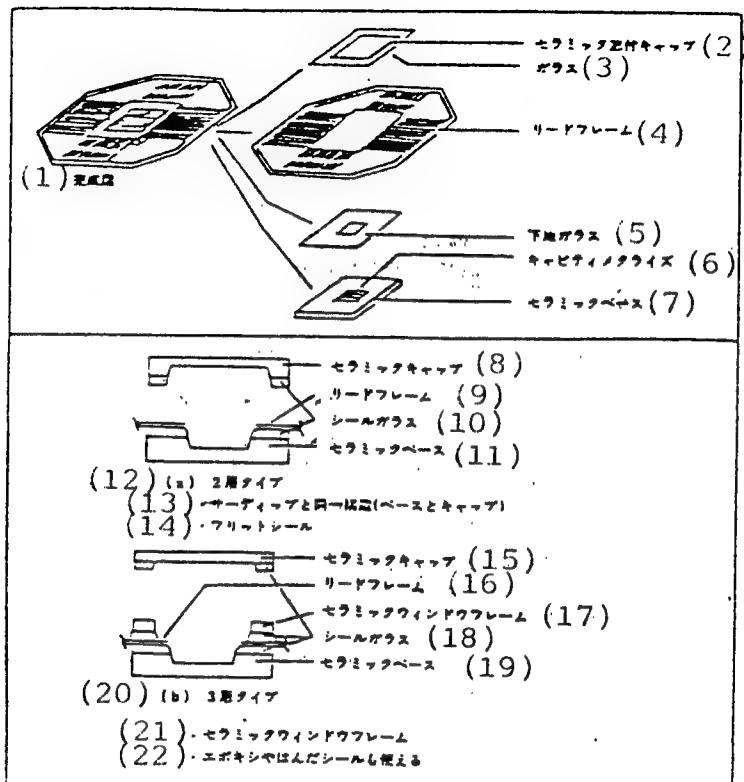
3. Recent Package Trends

The recent trends in ceramic packages can be summarized in terms of certain keynotes and demands. Specifically, the keynotes are *lighter, thinner, shorter, and smaller*. This trend is not likely to cease.

The demands which these keynotes give rise to are as follows.

- Implement many functions in the packages (or in the semiconductor elements).
- Develop single-surface-mounting models of packages which can be mounted directly to printboards.
- Raise the level of semiconductor integration.
- Run semiconductor devices at high speeds.
- This will result in the need to dispose of the heat that is generated when semiconductor devices are run at high speeds.
- As always, reduce prices.

Figure 4 QUAD CER PAC Structures



Key:

1. [illegible]	2. Ceramic [illegible] cap
3. Glass	4. Lead frame
5. Substrate glass	6. Cavity metalyze
7. Ceramic base	8. Ceramic cap
9. Lead frame	10. Seal[ing] glass
11. Ceramic base	12. (a) 2-layer type
13. Same structure as CER DIP (base and cap)	
14. Solid [legibility questionable] seal	
15. Ceramic cap	16. Lead frame
17. Ceramic window frame	18. Seal[ing] glass
19. Ceramic base	20. (b) 3-layer type
21. Ceramic window frame	22. Epoxy or solder seals also usable

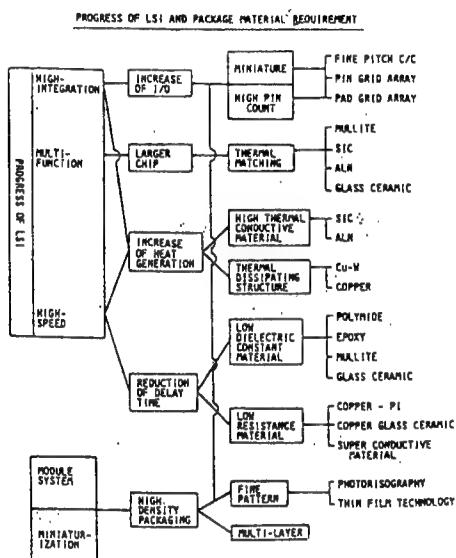
In general, semiconductor packages can be classified according to application into pin-insert mounting types and surface mounting types.

In terms of the numbers of packages demanded, there is a steady increase in the [relative] demand for the surface mounting type. This is reflected in Figure 5, which is a table of the surface mounting types that have recently been developed and put into production.

Fig 5 Recent Package Requirements

	pitch	50	100	200	400 (PIN COUNTS)
L	50 mil				
C	4.0	←	→		
C	2.5	←	→		
1.0, 0.5	5.0	←	→		
0.5, 0.25	4.0	←	→		
0.25	2.5	←	→		
QFP	5.0	←	→		
FL	5.0	←	→		
LE	2.5	←	→		
AA	2.5	←	→		
TD	2.0	←	→		
ED	2.0	←	→		
SO	2.5	←	→		
PGA	5.0	←	→		
PAD	—	—	—	←	→
ARRAY	—	—	—	—	—

Fig 6 Future Package Trends



4. Future Trends in Package Technology

In the context of future package trends, as LSI technology advances, there is a growing demand for various types of materials. As LSI technology progresses, higher levels of integration, greater functionality, and higher speeds are demanded, as are, in turn, more terminals (pins), and shorter delay times (Cf Figure 6).

This has resulted in the development of ways to cope with the demands for smaller sizes and more pins, ways to match coefficients of thermal expansion, materials of high thermal conductivity, efficient heat-radiating structures, low-dielectric materials, and low-resistance materials. Demands for increasingly smaller and modular systems, meanwhile, have led to high-density mounting, and, in the field of package fabrication, to the development of technologies for implementing superfine wiring (photolithography and thin-film technology) and multi-layer lamination.

Thus there are two main directions in which future package demand should develop.

(I) The trend toward greater demand for surface-mounting packages will intensify, stimulating the development of fine-pitch LACC packages, pad array packages, and QFP's.

(II) In the area of materials, package material combinations will be developed with better and better thermal and electrical characteristics in order to satisfy the demand for better and better performance.

In the area of single-chip packages, moreover, we should have increasingly realistic packages in the 200-500 pin class, made with combinations of various materials, including surface-mounting packages which employ the TAB (tape auto bonding) mounting technique.

SCIENCE & TECHNOLOGY POLICY

Japan Society for Promotion of Science Featured

90CF0073 Tokyo NIHON GAKUJUTSU SHINKOKAI JIGYO NO GAIYO in Japanese
May 89 pp 1-75

[Excerpt] Outline of FY89 Activities of Japan Society for Promotion of Science

Foreword by Montoku Sakai, Director of the Board, Japan Society for the Promotion of Science

The Japan Society for the Promotion of Science was established by law as a corporation with special status in September 1967, and as the core organization for the task of promoting science in Japan. Needless to say, the role that the nation plays in the promotion of science is extremely important. On the other hand, depending on the type of activity, there are aspects that are not necessarily responsive to handling by the government, and there are many areas where better results can be achieved through flexible management. That is why the Society was established as a corporation with special status.

The Society has developed the activities as planned when it was launched, and over the years, it also has started up new activities that it is endeavoring to complete. Despite the stringent state of the nation's budget, the Society's activities will continue to expand under its FY89 budget due to great efforts made in various sectors. One endeavor is the increase in appointments of special researchers. I believe that this will greatly enhance the task of nurturing young researchers with a wealth of originality, who bear on their shoulders the future of Japan's scientific research. Furthermore, as part of the promotion of international scientific exchange, we will endeavor to increase appointment of special researchers from abroad under a program launched in FY88, as well as increase the countries covered, thereby further improving the system for getting superior young foreign researchers.

It also is of great significance that new research liaison centers have been established in Bangkok and Sao Paulo, which brings the total number of centers to four.

As for scientific cooperation with the developing countries, since 1978, the Society has carried out exchange of researchers, joint research, seminars and other forms of exchange with Thailand, Indonesia, the Philippines, Singapore and Malaysia. In FY89, we will commence exchange, using key universities, with Indonesia in the field of bioscience, with Thailand in oceanography and with Singapore in medical science. We also will try to expand assistance to Ph.D. aspirants.

Scientific cooperation with the developing countries to nurture young researchers will be expanded to include countries that are not members of the Association of Southeast Asian Nations (ASEAN). It has been decided that, in the first fiscal year, the program will be implemented with Argentina and Bangladesh.

In addition to the above, we want to find various ways to manage activities as a whole more effectively, smoothly and completely. We ask the understanding and cooperation of all the relevant parties in this endeavor.

This document introduces in summary form all the activities of the Society. Its purpose is to assist researchers who wish to participate in any of the activities. We welcome your views on the content of this document.

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Synopsis of FY89 Activities (front flyleaf)

Synopsis of Researcher Exchange by Country and by Project (back flyleaf)

I. Summary of Activities

The society is a corporation with special status which, with the goal of contributing to scientific development, has been instrumental in aiding scientific research, assisting researchers, promoting the implementation of international scientific cooperation, and other endeavors to promote science. Its activities covers a broad area and can be summarized as follows by purpose of activity:

1. Aid for nurturing of researchers: Special researchers; special researchers (cancer); special foreign researchers
2. Promotion of social cooperation and tie-ups in the sciences: Comprehensive research; liaison council; R&D experts committee; industry-universities cooperative research
3. Promotion of international scientific cooperation
 - A. General international exchange: Invitation to foreign researchers; sending Japanese researchers abroad; international joint research meetings
 - B. Bilateral scientific exchange: Research exchange (researchers sent to specified countries); joint research and seminars (Japan-U.S. and Japan-France scientific cooperation)
 - C. Scientific exchange with developing countries: Exchange through key universities; assistance to Ph.D. aspirants; exchange via general exchange formula

4. Assistance to patent activities of national universities: Government-owned patent applications and maintenance; implementation of government-owned patents
5. Collection and provision of scientific information and dissemination of research results: Collection and provision of researcher data; publication of scientific books and monthly journals; use of scientific films produced by the Society
6. Endowments: Acquisition of domestic endowments for scientific promotion; individual endowments (Kaya conference, Oji seminar); endowments for overseas scientific cooperation
7. Other activities: International biology award; Prince Chichibu commemorative scholarship; handling of UNESCO coupons; fund-raising for convening of international scientific conferences

The following is a brief explanation of each project, giving such information as the basic activity, area covered, scale of work, and qualifications for applicants.

1. Air for Nurturing of Researchers

In view of the importance of nurturing researchers, the Society created a special researcher system in FY89 in accordance with the report of the Science Council on 6 February 1984, "concerning a basic policy to improve our scientific research system."

In FY84, the Society continued to carry out the special researcher (cancer) system in accordance with the "10-year comprehensive cancer strategy," a 7 June 1983 decision of the Cabinet conference on measures to fight cancer.

Also, exclusive assignment to long-term research abroad in outstanding universities and other scientific research institutions is an extremely effective way to nurture researchers with rich international vision. Therefore, since FY82, we have been implementing an overseas special researcher program.

[rest of section omitted]

2. Promotion of Social Cooperation and Tie-Ups in the Sciences

Since 1933, the Society has set up industry-universities cooperation committees composed of first-ranking researchers in each research topic to act as an intermediary between industry and the universities. It has played a unique role in selecting topics that are important to technical development and in holding numerous consultations on research, information exchanges, and the like.

In recent years, there has been a rapid increase in a broad range of requests for scientific research from various sectors of society, not just from industry. Therefore, in FY82, the "comprehensive research liaison council" and the "R&D experts committee" were established to enhance the existing activities of the "industry-universities cooperative research committee," as vehicles for exploring new areas of industry-universities cooperation, and efforts are being made to further promote social cooperation and tie-ups.

[rest of section omitted]

3. Promotion of International Scientific Exchange

Progress in scientific research which inherently is of an international nature is promoted through active international exchange. Since its establishment, the Society has stressed the expansion of activity in this area, and further development is anticipated as one essential function of the promotion of science.

The Society's activities in international scientific exchange can be divided into three main types. The first is "general international exchange," wherein applications from Japanese researchers are used as the basis for promoting broad exchanges with researchers in many countries in all scientific areas. The second is "bilateral scientific exchange," which is based on bilateral agreements with specific countries. The third is "scientific exchange with developing countries," which is part of bilateral exchange but covers developing countries in particular.

International exchange activities can be divided into three modes: Researcher exchange (inviting foreign researchers to Japan and sending Japanese researchers abroad); joint international research (including the exchange of scientific data and materials); and international research meetings (such as seminars).

[rest of section omitted]

4. Assistance in Patent Activities at National Universities

Since April 1978, the Society has overseen government-owned patents, from application to implementation, that have resulted from discoveries by instructors of national universities, junior colleges and institutes used jointly by national universities. This follows the intent of the report of the Ministry of Education's Science Council, "concerning the handling of patents for discoveries by university instructors," dated 17 June 1977. In the past, each university had the task of handling patent application, maintenance and implementation for its staff. This has been centralized under the society for quicker, more accurate handling, and was arranged to protect and effectively use patent rights and promote broad scientific research that consolidates individual discoveries.

[rest of section omitted]

5. Collection and Provision of Scientific Data and Dissemination of Research Results

In its collection and provision of scientific data, the Society emphasizes data concerning researchers and research institutions and research trends and results. It prepares databases on researchers and research institutions, publishes "handbook of university research centers," "synopsis of researchers and research topics," and the "science monthly" journal. Also, to disseminate research results, the Society publishes scientific books and loans out scientific films produced by the Society.

Record of Researcher Exchanges by Country and Activity

Japan Society for the Promotion of Science

Activity Fiscal Year	Accepting													Total				
	Foreign Researchers Invited						Special Foreign Researchers (Youths from Advanced countries)			Bilateral Scientific Exchanges			Scientific Exchanges with the LDCs					
	Short Term			Long Term														
Country or Region	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88
Total	213	228	240	77	82	75	60	72	112	380	384	395	451	444	567	1181	1210	1389
Asia	23	24	34	28	34	35				194	164	172	451	444	567	696	666	808
East Asia	15	12	23	12	21	18				171	143	146				198	176	187
Southeast Asia	2	3	1	4	1	4							451	444	567	457	448	572
South Asia & Southwest Asia	6	9	10	12	12	13				23	21	26				41	42	49
Oceania	8	5	7	1	2	1				7	8	10				16	15	18
Africa		2	3		1	4										3	7	
Europe	92	113	97	24	19	20	60	72	97	138	168	174				314	372	388
Western Europe	85	98	81	13	9	10	60	72	97	92	115	117				250	294	305
Eastern Europe & Soviet Union	7	15	16	11	10	10				46	53	57				64	78	83
North America	89	84	94	20	24	13			15	33	30	27				142	138	149
Latin America	1		5	4	2	2				8	14	12				13	16	19

(By Country Breakout)

Asia	China	11	9	17	8	17	15			137	105	113				156	131	145
	South Korea	4	3	5	4	4	3			34	38	33				42	45	41
	(Hong Kong)		1													1		
	Indonesia												124	113	145	124	113	145
	Malaysia			2	1	3							36	38	53	38	39	56
	Philippines												79	86	110	79	86	110
	Singapore												52	44	68	52	44	68
	Thailand	2	2		2								160	163	191	164	165	191
	Vietnam		1	1			1									1	2	
	Bangladesh				1		1									1	1	
S Asia & SW Asia	India	4	4	4	6	8	9			21	19	24				31	31	37
	Iran				2											2		
	Israel	2	4	6		1				2	2	2				4	7	8
	Nepal				2	1										2	1	
	Sri Lanka																	
	Turkey				1	2	3									1	2	3
	Syria		1													1		
Oceania	Australia	7	3	3	1	1	1			7	8	10				15	12	14
	New Zealand	1	2	4		1										1	3	4

Activity Fiscal Year		Dispatched														Total			
		Special Researchers Sent Overseas			Japan-US S&T Cooperation Acty			International Joint Research			Bilateral Scientific Exchanges			Scientific Exchanges with the LDCs					
Country or Region	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88	
Total	30	32	33	314	359	315	214	250	204	535	619	517	382	447	451	1475	1707	1520	
Breakout by Region	Asia	1	2	1				68	99	58	67	89	57	382	447	451	518	637	567
	East Asia	1	2	1				39	58	37	53	71	42				93	131	80
	Southeast Asia						24	35	18				382	447	451	406	482	469	
	South Asia & Southwest Asia						5	6	3	14	18	15				19	24	18	
	Oceania	2	2	1				12	11	15	8	8	9				22	21	25
	Africa	1	1	1			2			7	6	9				10	7	10	
	Europe	9	11	10			87	100	95	164	172	138				260	283	243	
	Western Europe	9	11	10			82	94	87	135	141	107				226	246	204	
	Eastern Europe & Soviet Union						5	6	8	29	31	31				34	37	39	
	North America	17	16	20	314	359	315	45	40	33	283	332	294				659	747	662
	Latin America									3	6	12	10				6	12	13

(By Country Breakout)

Asia	E Asia	China	1	1				13	31	19	43	53	27				57	85	46
		South Korea	1	1				25	27	18	10	18	15				35	46	34
		(Hong Kong)					1									1			
		Indonesia												97	117	122	97	117	122
		Malaysia					1	13	11					30	36	43	31	49	54
		Philippines				8								88	72	90	96	72	90
		Singapore			2	1								36	69	43	38	70	43
		Thailand			13	21	7							131	153	153	144	174	160
		Vietnam																	
		Bangladesh																	
	SE Asia & SW Asia	India			3	3		10	15	10						13	18	10	
		Iran					1			3	2	2				3	3	2	
		Israel																	
		Nepal																	
		Sri Lanka					3											3	
	South & SW Asia	Turkey			2	2		1	1	3						3	3	3	
		Syria																	
Oceania		Australia	2	2			4	4	6	8	8	9				14	14	15	
		New Zealand			1		8	7	9							8	7	10	

Activity Fiscal Year		Accepting												Total			
		Foreign Researchers Invited						(Youths from Advanced countries)			Bilateral Scientific Exchanges			Scientific Exchanges with the LDCs			
		Short Term		Long Term		86	87	88	86	87	88	86	87	88			
Country or Region		86	87	88	86	87	88										
Africa	Egypt		1													1	
	Nigeria			1			2									3	
	Kenya		1			1										2	
	Tanzania			1			1									2	
	Zaire			1			1									2	
Europe	Austria		2	3	1						12	12	10		13	14	13
	Belgium	1		3	1						1		3		3		6
	Denmark	1	2												1	2	
	Finland	2	1			1					6	5	5		6	7	7
	France	9	15	16	1	1	2	22	25	30	20	26	24		52	67	72
	FRG	25	35	23	5	3	1	22	27	32	14	13	13		66	78	69
	Greece	1				1	1								1	1	1
	Iceland		1													1	
	Ireland			1												1	
	Italy	3	4	2	1		1				12	20	13		16	24	16
	Malta			1												1	
	Netherlands	4	3	6	1						1	2	1		6	5	7
	Norway				1										1		
	Portugal	1	1		1	1									2	3	
	Spain	1		1	1	1									2	2	1
	Sweden	3	4	4							7	9	12		10	13	16
	Switzerland	4	7	3		1	3				2		1		6	8	7
	United Kingdom	32	22	17		1	1	16	20	35	17	28	35		65	71	88
Europe & Soviet Union	Bulgaria				1	1	1				6	8	10		7	9	11
	Czechoslovakia	1		1	1	2	2				2	4	3		4	6	6
	East Germany	2	3	1	1						4	4	3		5	7	6
	Hungary	2	2	2	1						8	9	11		11	11	13
	Poland	3	3	5	6	6	4				8	7	8		17	16	17
	Romania			2							2	1			2	3	
	Soviet Union	1	7	3			2				18	19	21		19	26	26
	Yugoslavia		1		1		1								1	1	1
	Canada	13	5	11	4	5	2				17	19	15		34	29	28
	United States	76	79	83	16	19	11				15	16	11	12	108	109	121
America	Latin A	Argentina		2	1							4			1	4	2
		Brazil		2	3	2	1				2	6	9		5	8	12
		Mexico			1		1				6	4	3		6	4	5
		Peru	1												1		

Note: 1. The figures under "Bilateral Scientific Exchanges" accepted do not include foreign researchers who came to Japan to participate in research symposia or implement joint research.

2. The figures under "Bilateral Scientific Exchanges" dispatched include researchers sent overseas to the Napoli Coastal Laboratory, the International Center for Insect Physiology and Ecology (ICIPE), and the West Asian and African regions, and for joint research and seminars.

Activity Fiscal Year		Dispatched												Total				
		Special Researchers Sent Overseas			Japan-US S&T Cooperation Acty			International Joint Research			Bilateral Scientific Exchanges			Scientific Exchanges with the LDCs				
Country or Region	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88	86	87	88
Africa	Egypt									1	2	3				1	2	3
	Nigeria																	
	Kenya																	
	Tanzania	1	1	1						6	4	6				6	4	6
	Zaire						2	2								1	1	1
Europe	Austria						1			9	8	8				10	8	8
	Belgium						3	1		4	5	3				7	6	3
	Denmark																	
	Finland						1				2	3				1	2	3
	France	2	3	3			4	11	7	34	38	17				40	52	27
	FRG						25	26	30	52	49	43				70	75	73
	Greece								3									
	Iceland																	3
	Ireland																	
	Italy	1	1				6	5	10	6	9	6				13	15	16
	Malta																	
	Netherlands	1	2	2			4	2		3	2	2				8	6	4
	Norway								3									3
	Portugal																	
	Spain																	
	Sweden						7	11	8	5	6	3				12	17	11
	Switzerland	1	1	1			12	9	10	3	3	4				16	13	15
	United Kingdom	4	4	4			19	27	16	19	19	18				42	50	38
Latin America	Bulgaria							2	1	1	2					1	1	4
	Czechoslovakia																	
	East Germany																	
	Hungary						3	4	4	4	4	3				7	8	7
	Poland									6	5	5				6	5	5
	Romania								3	3	3					3	3	3
	Soviet Union						2	2	2	15	18	18				17	20	20
	Yugoslavia																	
	Canada	1	1				20	12	5	13	11	9				34	24	14
	United States	16	15	20	314	359	315	25	28	28	270	321	285				625	723
Asia	Argentina											2						
	Brazil							3	5	8	7				5	8	10	
	Mexico								1	4	1				1	4	1	
	Peru																	

Japan Society for the Promotion of Science FY90 Activities

1. Joint Research

Activity	Field	Items Scheduled for Adoption	Execution Period	Reciprocating Organization		Application Acceptance Period
				Yes	No	
Japan-U.S. Joint Scientific Research	Natural Science	Approx 20	Start between Jan & Dec 1990, complete within 2 years	X		1-31 May 1989
Japan-U.S. Educational and Cultural Research	Humanities and Social Science	2-3	Start btwn Apr 90 & Mar 91, complete within 2 years	X		
Japan-France Joint Scientific Research	Humanities, Social and Natural Science	1-2	Start btwn Apr & Dec 1990, complete within 2 years	X		
Joint International Research	Humanities, Social and Natural Science	Approx 29	Start Apr 1990 Complete within 2 years		X	

2. Research Symposia

Activity	Field	Items Scheduled for Adoption	Execution Period	Reciprocating Organization		Application Acceptance Period
				Yes	No	
Japan-U.S. Science Seminar	Natural Science	Approx 20	Btwn Apr 90 and Mar 91, in Japan or the U.S.	X		1-31 May 1989
Japan-U.S. Education and Culture Seminar	Humanities and Social Science	1-2	Btwn Apr 90 and Mar 91, in Japan or the U.S.	X		
Japan-France Science Seminar	Humanities, Social and Natural Science	Approx 2	Btwn Apr 90 and Mar 91, in Japan or France	X		
International Research Seminar	Humanities, Social and Natural Science	Approx 17	Btwn Apr 90 and Mar 91, in Japan		X	
Oji Seminar	Natural Science	1-2	Btwn Apr 90 and Mar 91, in Japan		X	

Joint research Research and Cooperation Department

Research symposia..... Research and Cooperation Department

Researcher exchanges..... Personnel Exchange Department

Other dispatch of researchers.... Research and Cooperation Department

Domestic activities..... Activities Department

Japan Society for the Promotion of Science (Tel: (03) 263-1721)
Yamato Building, Kojimachi 5-3-1, Chiyoda-ku, Tokyo-to, 102

3. Researcher Exchange

Activity	Field	Number of People to be appointed	Execution Period	Reciprocating Organization		Application Acceptance Period
				Yes	No	
[Invitation Activities] Invited Foreign Researchers (short term)	Humanities, Social and Natural Science	Approx 210	Between Apr 90 and Mar 91		X	1st period: 1-31 May 1989 2nd period: 1-30 Sep 1989
Invited Foreign Researchers (long term)	Humanities, Social and Natural Science	Approx 60	Between Apr 90 and Mar 91		X	1-30 Sep 1989
Special Foreign Researchers	Humanities, Social and Natural Science	Approx 30	Between Apr 90 and Mar 91		X	1-30 Sep 1989
[Dispatch Activities] Researchers Sent to Specific Countries	Differs by country	See note below	Between Apr 90 and Mar 91	X		1-31 May 1989
Special Researchers Sent Overseas	Humanities, Social and Natural Science	Approx 10	Sent btwn Oct 90 & Feb 91 for period of 2 years		X	1-10 Jul 1989

4. Other Dispatches of Researchers

Activity	Field	Number of People to be Appointed	Execution Period	Reciprocating Organization		Application Acceptance Period
				Yes	No	
Overseas Regional Research Center	Humanities, Social and Natural Science of the Region to which Sent	Nairobi: 2 Cairo: 1 Angola: 1	Apr 90 - Mar 91		X	1-30 Jun 1989

5. Domestic Activities

Activity	Field	Number of People to be Appointed	Execution Period	Application Acceptance Period
Special Researchers	Humanities, Social and Natural Science	Approx 500	Apr 90 - Mar 92	1-10 Jul 1989

Number of Researchers Expected to be Dispatched to Specific Countries

Australia (8)	Finland (3)	South Korea (13)	United Kingdom (15)
Austria (9)	France (12)	Mexico (4)	United States (2)
Belgium (4)	West Germany (6)	Poland (5)	Indonesia
Brazil (7)	Hungary (5)	Rumania (5)	Malaysia
Bulgaria (5)	India (9)	Sweden (5)	Philippines
Canada (7)	Israel (2)	Switzerland (2)	Singapore
China (52)	Italy (6)	Soviet Union (21)	Thailand
			Several

Note: Figures are subject to change based upon consultations with reciprocating organizations.

- END -

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